

BULLETIN
DE
L'ACADÉMIE POLONAISE
DES SCIENCES

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Rédacteur en chef suppléant
S. KULCZYŃSKI

CLASSE TROISIÈME

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L. INFELD

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K. BORSUK, S. LESZCZYCKI, J. SAMSONOWICZ, M. ŚMIAŁOWSKI

VOLUME I
NUMÉRO 7

VARSOVIE 1953

PRINTED IN POLAND

PAŃSTWOWE WYDAWNICTWO NAUKOWE — WARSZAWA 1953

Nakład 1.150 egz. + 50 odb.	Rękopis dostarczono 7. X. 1953
Ark. wyd. 4°1, druk. 4	Podpisano do druku 18. XII. 1953
Papier bezdrzewny sat. 70 g III kl.	Druk ukończono 30. XII. 1953
Format 70×100 cm	Zam. prod. 513/53 Cena zł 5,—

KRAKOWSKA DRUKARNIA NAUKOWA, KRAKÓW, UL. CZAPSKICH 4

A Lemma Concerning Recursive Functions and Its Applications

by

A. MOSTOWSKI

Communicated by K. KURATOWSKI at the meeting of June 22, 1953

1. Lemma. For every general recursive function $F(n)$ there is a primitive recursive function $H(n)$ such that

$$(1) \quad H(n) \leq H(n+1) \quad \text{for } n = 0, 1, 2, \dots,$$

$$(2) \quad \lim H(n) = \infty \quad \text{for } n \rightarrow \infty,$$

$$(3) \quad FH(n) \text{ is primitive recursive}^*).$$

Proof. Represent F in the form

$$(4) \quad F(n) = Q\{\mu x[R(x, n) = 0]\}$$

where μ denotes the "least number operator", Q and R are primitive recursive and R satisfies the condition

$$(5) \quad (n)(\exists x)[R(x, n) = 0]**).$$

Let $K(n)$, $L(n)$ be primitive recursive functions such that the formula $n \leftrightarrow (K(n), L(n))$ represents a one-one mapping of integers onto pairs of integers and put

$$(6) \quad X = E_n[R(K(n), L(n)) = 0].$$

The set X is primitive recursive. Hence it can be enumerated by a primitive recursive function $S(n)$ (repetitions not excluded).

We define now by a simultaneous recursion two functions $G(n)$ and $H(n)$:

$$(7) \quad G(0) = KS(0), \quad H(0) = LS(0),$$

$$(8) \quad G(n+1) = \begin{cases} G(n) & \text{if } LS(n+1) \leq H(n), \\ KS(n+1) & \text{if } LS(n+1) > H(n), \end{cases}$$

$$(9) \quad H(n+1) = \begin{cases} H(n) & \text{if } LS(n+1) \leq H(n), \\ LS(n+1) & \text{if } LS(n+1) > H(n). \end{cases}$$

*) By $FH(n)$ we denote the compound function $F(H(n))$.

***) We shall express this condition by saying that the μ -operation in (4) is effective.

It is obvious that the functions G and H are primitive recursive. We shall show that H satisfies the conditions (1)–(3).

(1) follows immediately from (9).

Let us assume that (2) is false, i. e., that there is an integer n_0 such that $H(n+1) = H(n)$ for $n \geq n_0$. It follows that $LS(n+1) \leq H(n)$ for $n \geq n_0$ and hence $LS(n+1) \leq H(n_0)$ for $n \geq n_0$. If $n < n_0$, we have by (9) and (1) either $LS(n+1) \leq H(n) \leq H(n_0)$ or $LS(n+1) = H(n+1) \leq H(n_0)$ and since $LS(0) = H(0) \leq H(n_0)$ we obtain the inequality $LS(n) \leq H(n_0)$ for all n . We shall show that this inequality entails a contradiction.

By (5) there is an x such that $R(x, H(n_0) + 1) = 0$. If p is such that $K(p) = x$ and $L(p) = H(n_0) + 1$, we have by (6) $p \in X$ and hence $p = S(q)$ for some q . Hence $LS(q) = H(n_0) + 1 > H(n_0)$. Formula (2) is thus proved.

From (7)–(9) we obtain by induction on n

$$R(G(n), H(n)) = 0 \quad \text{for } n = 0, 1, 2, \dots,$$

whence

$$(10) \quad FH(n) = Q\{(\mu x)[R(x, H(n)) = 0]\} = Q\{(\mu x)_{G(n)}[R(x, H(n)) = 0]\}$$

where $(\mu x)_{G(n)}[\dots]$ denotes the least integer $x \leq G(n)$ satisfying the condition $[\dots]$. It is known that if R is primitive recursive, then so is $(\mu x)_z[R(x, n) = 0]$. Hence (3) follows from (10) and the lemma is proved.

2. According to a definition due to S. Mazur a real number a ($0 < a < 1$) is called *general recursive* if there exist general recursive functions $U(n)$, $V(n)$ such that

$$\left| a - \frac{U(n)}{V(n) + 1} \right| < \frac{1}{n + 1} \quad \text{for } n = 0, 1, 2, \dots$$

This definition is known to be equivalent to the following*): There is a general recursive function $W(n)$ such that

$$(11) \quad \begin{aligned} W(n) = 0 \text{ or } W(n) = 1 \quad & \text{for } n = 0, 1, 2, \dots, \\ a = \sum_{n=1}^{\infty} \frac{W(n)}{2^n}. \end{aligned}$$

Theorem 1).** For every general recursive real number a ($0 < a < 1$) there are primitive recursive functions $M(n)$, $N(n)$, $P(n)$ such that

$$(12) \quad \begin{aligned} \lim_{n \rightarrow \infty} P(n) = \infty \quad & \text{for } n \rightarrow \infty, \\ \left| a - \frac{M(n)}{N(n) + 1} \right| \leq \frac{1}{P(n) + 1} \quad & \text{for } n = 0, 1, 2, \dots \end{aligned}$$

Proof. Denote by p_j the j -th prime and put

$$F(n) = p_1^{W(1)} p_2^{W(2)} \dots p_n^{W(n)}.$$

The function F is general recursive.

Let H satisfy (1), (2), (3) and let $\exp_k(m)$ denote the exponent of p_k in the expansion of m into the product of primes. The function $\exp_k(m)$ is

*) This equivalence has been proved by Prof. S. Mazur in a paper not yet published; cf. also [1].

**) This theorem answers a question communicated to me by Prof. S. Mazur.

known to be primitive recursive and we have

$$(13) \quad W(j) = \exp_j(FH(n)) \quad \text{for } j \leq H(n).$$

Now we define $M(n)$, $N(n)$, and $P(n)$ as follows:

$$(14) \quad \begin{cases} M(n) = \sum_{j=1}^{H(n)} 2^{H(n)-j} \exp_j(FH(n)), \\ N(n) = 2^{H(n)} - 1, \quad P(n) = 2^{H(n)}. \end{cases}$$

These functions are obviously primitive recursive. From (13) it follows that

$$\frac{M(n)}{N(n)+1} = \sum_{j=1}^{H(n)} \frac{W(j)}{2^j},$$

whence the theorem follows by (2), (11), and (14).

It is also easy to see that, conversely, if (12) holds with primitive recursive $M(n)$, $N(n)$, $P(n)$, then a is general recursive.

Theorem 2. *Let $\Phi(k, n)$ be a general recursive function universal for the class of primitive recursive functions. Then the set $Y = E_k[\lim_{n \rightarrow \infty} \Phi(k, n) = \infty]$ is not recursively enumerable.*

Proof. We shall show that if the set Y were recursively enumerable, there would exist a function $F(n)$ for which the lemma would be false. Let us therefore assume that Y is recursively enumerable and let S be a general recursive function which enumerates Y . Put

$$\Psi(k, n) = \max_{j \leq n} \Phi(S(k), j).$$

The function Ψ is general recursive. It is easy to show that it is universal for the class of primitive recursive functions satisfying conditions (1) and (2).

Put

$$E(n) = n - [\sqrt{n}]^2, \quad Q(n) = [\sqrt{n}]$$

and define a function T by induction as follows:

$$(15) \quad T(n) = (\mu x) \{ (u)_n [\Psi(E(n), x) \neq \Psi(E(u), T(u))] \}$$

where $(u)_n[\dots]$ means that the condition $[\dots]$ holds for every $u < n$. According to (15) the initial value of T is $T(0) = 0$.

The function T is general recursive. Indeed, we have for an arbitrary n

$$\lim_{x \rightarrow \infty} \Psi(E(n), x) = \infty$$

and hence there is an x such that

$$\Psi(E(n), x) \neq \Psi(E(u), T(u)) \quad \text{for } u < n.$$

Hence the μ -operator in (15) is effective and it is known that the induction-

schema combined with the effective μ -operation does not lead outside the class of general recursive functions.

Put

$$(16) \quad U(n) = \Psi(E(n), T(n)).$$

It follows from (15) that

$$U(m) \neq U(n) \quad \text{for} \quad m \neq n.$$

We shall show that the equation

$$(17) \quad U(x) = k$$

has a solution for every k .

Indeed, let q be the least integer such that $\Psi(q, 0) = k$. Put $n = \lceil \frac{1}{2}(q+1) \rceil^2 + q$ in (15). Since $E(n) = q$ we infer from (15) that if (17) has no solution $x < n$, then $T(n) = 0$ and hence by (16) $U(n) = \Psi(q, 0) = k$. Thus (17) has a solution $x \leq n$.

It follows from what we have proved that U enumerates the set of all integers without repetitions.

Now we put

$$(18) \quad V(k) = (\mu x)[U(x) = k],$$

$$(19) \quad F(k) = 1 \div \Phi(QV(k) \div [\tfrac{1}{2}(EV(k) + 1)], TV(k)).$$

These functions are obviously general recursive.

Taking $k = U(n)$ in (19) we get by (18)

$$(20) \quad FU(n) = 1 \div \Phi(Q(n) \div [\tfrac{1}{2}(E(n) + 1)], T(n)) \quad \text{for} \quad n = 0, 1, 2, \dots$$

Now assume that there is a primitive recursive function H satisfying (1), (2), (3). Since Ψ is a universal function for the class of primitive recursive functions satisfying (1) and (2) we infer that there is a q such that $H(n) = \Psi(q, n)$ for all n . Similarly there is an integer l such that $FH(n) = \Phi(l, n)$ for all n . Hence

$$(21) \quad F\Psi(q, n) = \Phi(l, n) \quad \text{for} \quad n = 0, 1, 2, \dots$$

In particular this equation holds for $n = T(n_0)$ where

$$n_0 = (\lceil \tfrac{1}{2}(q+1) \rceil + l)^2 + q.$$

Since $q = E(n_0)$, $Q(n_0) = \lceil \tfrac{1}{2}(q+1) \rceil + l$ we obtain from (21)

$$F\Psi(E(n_0), T(n_0)) = \Phi(Q(n_0) \div [\tfrac{1}{2}(E(n_0) + 1)], T(n_0)).$$

and since the left hand side is equal to $FU(n_0)$ we obtain

$$FU(n_0) = \Phi(Q(n_0) \div [\tfrac{1}{2}(E(n_0) + 1)], T(n_0)).$$

Comparing this result with (20), we get $FU(n_0) = 1 \div FU(n_0)$ which is impossible. Theorem 2 is thus proved.

The set Y of theorem 2 is evidently a $\Pi\Sigma$ -set, i. e., it can be defined by a formula of the form $(x)(\exists y)B(n, x, y)$ where B is recursive. The problem whether this set is at the same time a $\Sigma\Pi$ -set remains open.

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The Problem of »Equivalent« Potentials in Classical Equations of Motion

by

J. WERLE

Communicated by L. INFELD at the meeting of May 18, 1953

In this paper we consider the classical non relativistic equations of motion of a particle in an external electro or meso-static field. In all cases considered here these equations have the form

$$(1) \quad m \frac{d^2 \xi^k}{dt^2} = - \left(\frac{\partial \varphi}{\partial x^k} \right)_{x^k = \xi^k(t)} \quad (k = 1, 2, 3)$$

where the functions $\xi^k(t)$ describe the trajectory of the particle, and φ denotes its potential energy. The above equations are of course only approximative to the relativistic equations of motion, which have in general a much more complicated form

$$(2) \quad mc^2 \frac{d^2 \xi^\alpha}{ds^2} = F^\alpha \left(\varphi, \frac{\partial \varphi}{\partial x^\mu}, \frac{d\xi^\mu}{ds}, \frac{d^2 \xi^\mu}{ds^2} \right)_{x^\mu = \xi^\mu} \quad (\alpha = 1 \dots 4)$$

where $ds = c \sqrt{1 - \frac{v^2}{c^2}} dt$. The first three equations (2) for $\alpha = k$ are independent. The fourth, describing the conservation of energy, follows from them.

The range validity (1) is limited to small velocities and energies of the particle. The equations (1) do not account for the so-called relativistic phenomena, which follow from the strict equations (2). E.g. in the case of a constant Coulomb potential the relativistic equations lead to such effects as perihelion motion (the orbits are rosettes or deformed hyperbolas), and the motions on spirals towards or from the centre according to the value of orbital momentum etc. None of these effects is given by (1). It is well known that the orbits described by (1) are ellipses, hyperbolas and parabolas only.

We ask if it is possible to retain the non relativistic form of (1) but with a modified potential $V(\varphi)$ instead of φ

$$(1') \quad m \frac{d^2 \xi^k}{dt^2} = - \left(\frac{\partial V}{\partial x^k} \right)_{x^k = \xi^k}$$

so as to obtain a better approximation to the relativistic equations (2). It appears that it is really possible to find such a potential $V = V[\varphi]$, which will account for many relativistic effects in agreement with (2). A potential of this type we shall call an »equivalent« potential. Of course we cannot expect absolute equivalence between (1') and (2). The expressions obtained for V describe very well the orbits of the particle in space, but the time dependence can reveal greater discrepancies. (E. g. equations of the form (1') give no relativistic restriction $|\dot{\xi}^k| < c$ on velocity).

We now deduce the form of the »equivalent« potential V for the case of a charged particle moving in an electrostatic field. This can be done by means of appropriate Hamilton-Jacobi equations, which are strictly equivalent to (1') or (2). In other words we seek such a V , which makes the non relativistic Hamilton-Jacobi equation

$$(3) \quad \frac{\partial S'}{\partial t} + \frac{1}{2m} (\nabla S')^2 + V = 0$$

the best approximation to the relativistic equation

$$(4) \quad -\frac{1}{c^2} \left(\frac{\partial S}{\partial t} + \varphi \right)^2 + (\nabla S)^2 + m^2 c^2 = 0.$$

If we put $S = -mc^2 t + S'$ into the last equation we get

$$(5) \quad -\frac{1}{c^2} \left(\frac{\partial S'}{\partial t} - mc^2 + \varphi \right)^2 + (\nabla S')^2 + m^2 c^2 \\ = 2 \left(m - \frac{1}{c^2} \frac{\partial S'}{\partial t} \right) \varphi + \left(2m - \frac{1}{c^2} \frac{\partial S'}{\partial t} \right) \frac{\partial S'}{\partial t} + (\nabla S')^2 - \frac{\varphi^2}{c^2} = 0.$$

The only terms which must be dropped in order to reduce (5) to the form

$$(3) \text{ are } -\frac{1}{c^2} \frac{\partial S'}{\partial t} \text{ in both brackets. Dividing by } 2m \text{ we finally get}$$

$$(6) \quad \frac{\partial S'}{\partial t} + \frac{1}{2m} (\nabla S')^2 + \varphi - \frac{\varphi^2}{2mc^2} = 0$$

therefore

$$(7) \quad V = \varphi - \frac{\varphi^2}{2mc^2}$$

Thus we see that, besides the usual expression φ , our V contains an additional term $-\frac{\varphi^2}{2mc^2}$, which is always negative. This term is equivalent to an additional force drawing the particle in the direction of the growing $|\varphi|$. This force is of course of entirely relativistic origin. For instance to

the Coulomb potential $\frac{e_1 e_2}{r}$ (repulsive or attractive) an additional purely attractive term $-\frac{e_1^2 e_2^2}{2mc^2} r^{\frac{1}{2}}$ must be added. Such a modified potential will lead to all the above-mentioned relativistic effects, describing the orbits of the particle in a very good agreement with (2) or (4), provided the energy is not too great. In order to establish the range of validity of (7) we must remember that we have dropped $\frac{\partial S'}{\partial t} = \varepsilon$, regarding it as being much smaller than mc^2 , i. e. we assume $\varepsilon \ll mc^2$. The smaller ε is, the smaller will be the deviations of the orbits obtained from (3) compared with those obtained from (4). If $\varepsilon = 0$ we get strict relativistic orbits.

The same reasoning applies in the case of the classical equations of the motion of a nucleon in a static vector meson field described by the static potential Φ . We obtain the same expression as in (7). E. g. in the case of a static Yukawa potential we get $V = g^2 \frac{e^{-\mu r}}{r} - \frac{g^4}{2mc^2} \frac{e^{-2\mu r}}{r^2}$. The additional term corresponds to a strong attractive force with a small range.

But the most interesting features are revealed by the static scalar meson field. From the usual Lagrangian of the scalar theory

$$(8) \quad L' = \int \varphi(\xi^k, t) \sqrt{1 - \frac{v^2}{c^2}} dt - mc^2 \int \sqrt{1 - \frac{v^2}{c^2}} dt$$

we obtain the following equations of motion: [1]

$$(9) \quad \frac{d}{ds} \left\{ (mc^2 - \varphi) \frac{d\xi^\alpha}{ds} \right\} = \left(\frac{\partial \varphi}{\partial x^\alpha} \right)_{x^\alpha = \xi^\alpha} \quad (\alpha = 1 \dots 4)$$

The corresponding Hamilton-Jacobi equation has now the form

$$(10) \quad -\frac{1}{c^2} \left(\frac{\partial S}{\partial t} \right)^2 + (\nabla S)^2 + \left(mc^2 - \frac{\varphi}{c} \right)^2 = 0.$$

By substituting $S = -mc^2 t + S'$ as before, and neglecting $\left(\frac{\partial S'}{\partial t} \right)^2$ we get

$$(11) \quad \frac{\partial S'}{\partial t} + \frac{1}{2m} (\nabla S')^2 - \varphi + \frac{\varphi^2}{2mc^2} = 0$$

The equivalent potential now has the form

$$(12) \quad V = -\varphi + \frac{\varphi^2}{2mc^2}$$

The relativistic additional term is now positive and therefore corresponds to a force, which pushes the particle in the direction of falling $|\varphi|$. If $|\varphi|$ is strong enough this relativistic force can prevail over the ordinary

force. Let us take as an example the Yukawa potential $\varphi = g^2 \frac{e^{-\mu r}}{r}$. Then we have

$$(13) \quad V = -g^2 \frac{e^{-\mu r}}{r} + \frac{g^4}{2mc^2} \frac{e^{-2\mu r}}{r^2}$$

This means that we have an additional strong repulsive potential of small range. The distance r_0 at which the attractive force changes into a repulsive one, can be found from the condition $\left(\frac{\partial V}{\partial r}\right)_{r=r_0} = 0$. It depends on the values of g and μ . With the normally adopted values $\mu \simeq 7 \cdot 10^{12} \text{ cm}^{-1}$ and $g \simeq 10e$ we obtain $r_0 \simeq 10^{-14} \text{ cm}$. At moderate energies the smallest possible separation (i. e. the radius of the repulsive core) is $\frac{1}{2} r_0$. The depth of the potential hole (13) is very insensitive to the changes of g . It has the value $\simeq \frac{1}{2} mc^2$.

Assuming the adiabatic theory of interaction we can extend these results to the case of two nucleons interacting through the scalar meson field. We can state that the relativistic equations of motion imply a strong repulsive force between two nucleons at distances of the order of 10^{-14} cm . If the binding energies satisfy the condition $\varepsilon \ll mc^2$, the nucleons behave like impenetrable spheres. As regards the sources of the meson or electromagnetic fields, they are nevertheless point sources.

The same conclusion can be drawn directly from a discussion of the relativistic equation (9). The change from attraction to repulsion is intimately connected with the change of sign of $(mc^2 - \varphi)$.

Let us briefly discuss how great a contribution we may expect from these relativistic terms in the theory of the atom and nucleus. E. g. if in (7) we take $\varphi = \frac{e^2}{r}$, (e and m denote now the charge and mass of the elec-

tron) we obtain for the distance at which the relativistic term $-\frac{e^4}{2mc^2} \frac{1}{r^2}$

is comparable with $\frac{e^2}{r}$ a value of the order of a classical electron radius i. e. 10^{-13} cm . This quantity is very small compared with atomic radii (10^5 times smaller). Nevertheless this effect should not be forgotten when one is determining the forces between two electrons at very small distances.

Much more important contributions are to be expected in the case of meson fields and nuclear phenomena. E. g. the radius of the repulsive core is at most only one order smaller than the range of nuclear forces. This result is all the more interesting in view of the fact that recent experiments on the scattering of fast nucleons on nucleons suggest the existence of such a repulsive core [2].

It can easily be proved that the same effects are inherent in the quantum theory of motion in a static potential. E. g. the Schrödinger equa-

tion for the electron in a static Coulomb field with potential (7) gives a part of the relativistic effects obtained from the Dirac equation.

But the quantitative agreement is not so good, as in the case of the classical equations of motion, because in the quantum theory we also have spin effects, which are of the same order as the contributions from $-\frac{\varphi^2}{2mc^2}$.

The same is true as regards the scalar meson field. Besides the repulsive central potential mentioned above we obtain non-central spindependent forces. Ignoring these repulsive forces while simultaneously retaining spin forces seems at any rate to be unjustified.

Institute of Theoretical Physics, University of Warsaw

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On the Monochromatical Excitation of the Fluorescence in Tetrahydrofluorocyclene Solutions

by

Z. MAŁKOWSKI

Communicated by S. PIENKOWSKI at the meeting of February 23, 1953

The band spectrum of the tetrahydrofluorocyclene solutions undergoes a twofold change. Firstly, the spectrum distribution along the wave-number axis changes with certain solvents, and secondly, the character of the spectrum changes with the wave length of the exciting light.

The largest shift in the fluorescence and absorption spectrum towards longer waves was observed in the case of a solution of the dye in carbon disulphide; this amounted to approx. 900 cm^{-1} [1]. The solution of this dye in carbon tetrachloride shows an apparent shift in the fluorescence spectrum towards longer wave-lengths. However, the position of absorption maxima does not change considerably when compared with the positions obtained by using other solvents, such as methanol, benzene, acetic acid, chloroform and xylene.

When this phenomenon was examined more thoroughly, it was proved that in CCl_4 a quickly-acting photochemical reaction takes place, resulting in the disappearance of the fluorescence in the short wave-length bands. It is worth noting also that with all the related dyes (biacene, fluorocyclene and its hydrogenized derivatives) a similar reaction takes place.

This photo-reaction progressing with time was tested by means of a very bright C1 Huet spectrograph. Fluorescence was excited monochromatically in two narrow spectral regions. In the region of the shorter wave-length (approx. 4000 Å) the unchanged dye was excited to typical blue and violet fluorescence. In the region of the longer wave-length (4300 Å) only the products of photo-reaction were excited and a greenish fluorescence was observed.

The monochromatical excitation of other solutions in amyl alcohol or benzene was studied, and my attention was drawn to a second type of change occurring in the fluorescence spectrum, viz. the division of the spectrum into several parts according to the wave-length of the exciting

light. In all the solutions, except the CCl_4 solution, the time factor did not effect any change in the character of the fluorescence spectrum. Therefore it may be concluded that no photochemical reaction exists in these cases. Nevertheless when excitation was confined to the long wave-length region a greenish fluorescence was observed. This fluorescence corresponds in character to the fluorescence of the photo-reaction products which was observed in CCl_4 .

In this brief note I shall present the results of the experiments in which monochromatical excitation was used for a number of wave-lengths

of the spectrum in tetrahydrofluorocyclene benzene solutions. A filament lamp was used as a source of light. Narrow strips of varying spectral width in some cases smaller than $25\text{\AA}$ were separated from the spectrum by means of a double Van Cittert glass monochromator. In Fig. 1 microphotograms are shown (from "a" to "h") representing the course of the change of the fluorescence spectrum at the antistokes excitation in the spectral region of I and II bands of the fluorescence spectrum. On the microphotograms the wave-length increases from right to left. The scattered light may be recognized in the form of a narrow band (*p*), the spectral position of which moves gradually in the direction of the increasing wave-length. As the beam of the exciting light passes, the character of the fluorescence spectrum changes. Bands I and II disappear simultaneously, but in band III an independent fluorescence was observed. The greenish

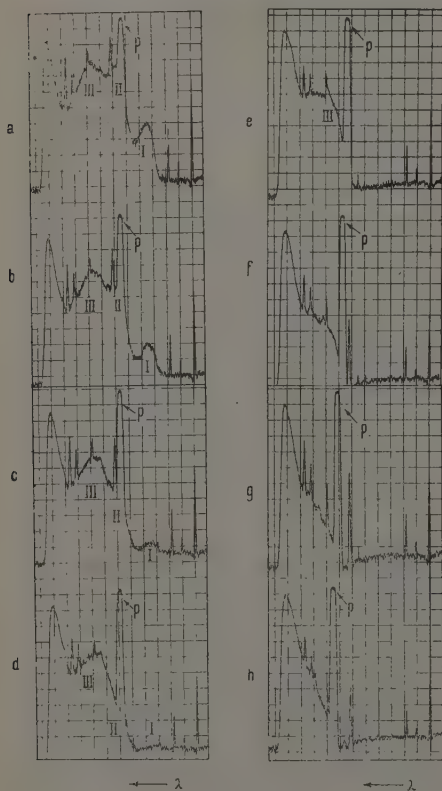


Fig. 1

fluorescence was so faint that exposure of the orthochromatical plates took several hours, whereas in the case of the blue-and-violet fluorescence excited in the long wave-length absorption band, several minutes sufficed for this purpose.

In the second series of experiments I was concerned with spectra monochromatically excited in the ultraviolet absorption bands. Excitation was

caused by lines of the following wave lengths: 4350, 4047, 3650, 3341, 3131 Å. A mercury lamp and a quartz monochromator were used. These experiments confirmed the independence of long wave-length fluorescence when excited by a 4350 Å line. Moreover, when the sample was excited by shorter wave-lengths I noticed a broadening of the fluorescence bands — a phenomenon hitherto unobserved. On account of reabsorption, the short wave-length region of the broadened band I was considerably deformed. Experimental conditions had to be suitably adjusted in order to obtain the maximum effect. In Fig. 2 are shown the overexposed microphotograms of the spectra excited by 4047 and 3131 Å lines. In the lower part of Fig. 2 are seen two microphotograms corresponding respectively to the normal (*a*) and to the overexposed (*b*) fluorescence spectrum excited by a 4047 Å line. In the upper part are seen two microphotograms (*c* and *d*) of the overexposed spectrum excited by a 3131 Å line. In the upper photogram, in order to make comparison possible, the short wave-length edge (*k*) of the fluorescence spectrum excited by a 4047 Å line, is drawn in. The irradiation with a 3131 Å line corresponded to the excitation in the absorption regions of the naphthylene groups [2]. In the region of minimum absorption i. e. the region between the naphthylene band and the long wave-lengths a broadening of band I was also observed as a result of excitation by a 3341 Å line.

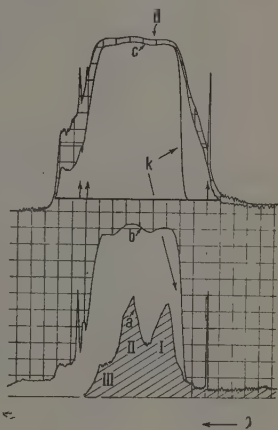


Fig. 2

The fact that band I broadens towards shorter wave-length and that there exists a marked "energy simplicity" of the fluorescence molecule may prove in view of the Nieporent classification [2], [3] that locally the higher vibrational states of the molecule are populated more completely and that a new short wave-length band, though strongly absorbed, has appeared. In my previous report [2] a simplified model of the electronic and vibrational transitions in the tetrahydrofluorocyclene molecule was presented (see [2] Fig. 3). The probable transition was indicated there by means of a dotted line. However, the fact that in the region of band III the excitation is independent, leads us to suppose that some added independent fluorescent substances may be present in the solution. The independent electronic transitions present in the tetrahydrofluorocyclene as well as the isomers coexisting in the solution must also be taken into consideration.

Light is thrown on the above problem by the investigations recently undertaken by J. Woźniak [4] who has discovered the separativeness of so-called naphthylene fluorescence. Her results are closely connected with the broadening of band I, previously observed in the course of my investigations. The experimental data concerning the above-mentioned facts are

set forth in Fig. 3. The absorption curve (*a*) is plotted against $\log \log 1/T$ and against the wave-number axis, and the microphotometric curve of the fluorescence spectrum (*f*), in which the broadening of the bands was observed, is also marked. A microphotometric dotted curve representing the green fluorescence (*e*) excited by a 4350 Å line may also be seen. In

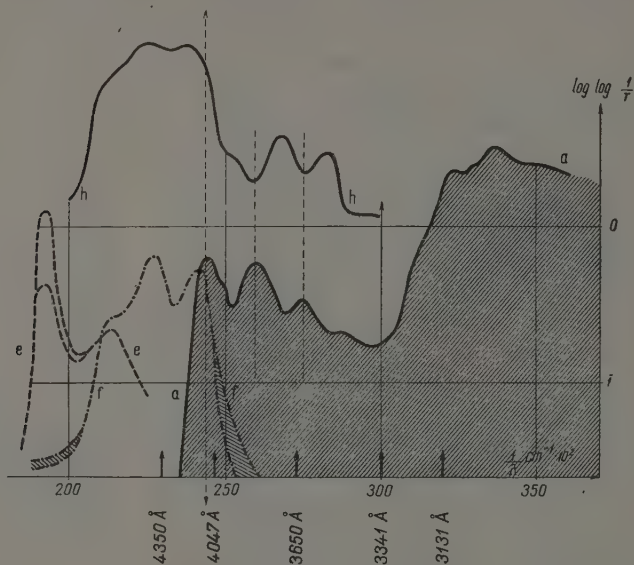


Fig. 3

the upper part a curve taken from J. Woźniak's report is shown after having been calculated in terms of wave-numbers. This curve represents the fluorescence spectrum (*h*) excited by a 3341 Å line and photographed by means of a quartz spectrograph. It can easily be seen that the structure of the spectrum separated from the fluorescence of the naphtylene groups is, in a certain sense, a negative of the absorption spectrum. The last diagram shows the connection between the above-mentioned broadening of band I and the short wave-length fluorescence that was observed by J. Woźniak.

The results obtained so far, viz. the peculiarity of the fluorescence in the region of band III and the broadening of band I towards the shorter wave-lengths, make a choice between the above-mentioned two interpretations of the experiments extremely difficult. According to the first interpretation the cause is to be found in the peculiar structure of the fluorescence molecule, whereas if we accept the second point of view, then the cause will be attributable to the important part played by the added fluorescent substances.

In the next investigations a combination of methods comprising both optical and chromatographical analysis, was used and the results thus obtained will be presented in further reports.

The author is much indebted to Profesor S. Pieńkowski for his encouragement and for the kind interest he took in this work.

Institute of Experimental Physics, University of Warsaw

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3.20 MeV γ -Radiation of ThD Determined by the Photographic Emulsion Technique

by

H. NIEWODNICZAŃSKI and M. WIELOWIEJSKA

Communicated by H. NIEWODNICZAŃSKI at the meeting of May 18, 1953

In the extensive scientific literature dealing with the subject of γ -radiation of radioelements of the thorium family there are only a very few remarks concerning the part of γ -rays spectrum of energy above that of the well known line at 2.62 MeV which is the strongest line in any thorium source.

In 1936, Alichanov, Alichanian and Kosodarev [1] reported on some traces of gamma radiation of the energy of about 3.2 MeV emitted by a ThC" source. They investigated the γ -ray spectrum by observing the magnetic spectrum of the electrons of pairs produced by γ -rays in Pb, Al and Be. In the same year Simons and Zuber [2] investigated the production of electron pairs in a cloud chamber filled with argon and methyl iodide by the γ rays from a RaTh source. Besides many electron tracks due to electron pairs produced by the γ -rays of 2.62 MeV they observed a few pairs giving some evidence of the existence of γ -ray photons of higher energy between 3.0 and 3.6 MeV.

Alichanov and Latyshev [3] carefully studied the high energy γ -ray spectrum obtained from a source of thorium C with its derivatives by measuring the energies of pair-produced positrons in a magnetic spectrometer. In the spectrum which they obtained a weak γ -ray line of the energy 3.20 MeV was also present. The relative intensity of this line with respect to the line at 2.62 MeV was found to be about 1/40.

Many of the more recent investigations concerning the thorium γ -ray spectrum (in some of which scintillation γ -ray detectors were also used) give no indication of the existence of a γ -ray line at 3.20 MeV.

In our experiments the spectrum of the γ -radiation of energy above 1.67 MeV emitted by a mesothorium sample was investigated by means of the photographic emulsion technique. The energy of the γ -ray photons was determined from the lengths of the proton recoil tracks in nuclear emulsion plates irradiated by photoneutrons originated in beryllium.

Fig. 1 represents the horizontal projection of the experimental arrangement. Gamma rays from a mesothorium source (of about 35 mC radium equivalent) were filtered in a 4.5 cm. lead layer and passed through a cylindrical channel of a diameter of 1.5 cm. in a lead block to a piece of metallic beryllium, approximately spherical in shape and about 0.9 cm. in diameter, situated in front of the opening in the lead channel. Three Ilford C2, 100 μ nuclear emulsion plates were situated as shown in Fig. 1, all of them being at the same distance from the centre of the piece of beryllium. The planes of each of the three plates were inclined at an exactly equal angle of 13° in respect to the horizontal plane of Fig. 1. The thickness of the lead filter used was found experimentally to be the most suitable for diminishing the soft γ -ray background in the photographic emulsion. The whole arrangement was surrounded by a layer of lead 10 cm. thick which is not shown in Fig. 1.

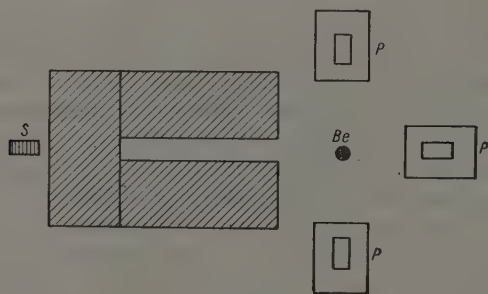


Fig. 1

Neutrons produced in beryllium in the photoreaction ${}^9\text{Be}(\gamma, n){}^8\text{Be}$, not having been slowed down, also entered the emulsion of the three exposed plates. Those neutrons which came into collision with hydrogen nuclei gave rise to proton tracks in the emulsion. The length of a track in the case of a head-on collision, in which the entire energy of the neutron is transferred to a proton, enables us to determine the energy of the colliding neutron. In our experiments the maximum lengths of proton tracks forming a small angle with the initial directions of neutron velocities indicate two distinctly different groups: a group with a length of about 12μ and a second much less numerous one with a length of 22μ . According to the range-energy curve for protons in C2 nuclear emulsions obtained by Rotblat [4], the lengths of these proton tracks correspond to their energies of about 0.88 MeV and of about 1.35 MeV which are also the energies of the two neutron groups. According to recent investigations carried out by Mobley and Laubenstein [5] and by Sher, Halpern and Mann [6] the value of the threshold energy of the reaction (γ, n) in beryllium nuclei is about 1.67 MeV. The conservation of momentum enables us to evaluate the energy of the recoil of the

^8Be nucleus in the photonuclear reaction. This energy is 0.12 MeV and 0.17 MeV for the neutron energies 0.88 MeV and 1.35 MeV respectively. Then, the energies of the γ -ray photons producing in beryllium photoneutrons of the two energies 0.88 MeV and 1.35 MeV are about 2.67 MeV and 3.19 MeV respectively. The figures obtained are very close to the values 2.62 MeV and 3.20 MeV and may be regarded as a confirmation of the existence of thorium γ -rays of the latter energy.

At the same time we tried to determine the ratio of intensities of the γ -ray lines at 3.20 MeV and at 2.62 MeV when emitted by the mesothorium source. For this purpose the following measurements were made. In order to diminish any possible error arising from different angular distributions of photoneutrons of two unequal energies three C2 plates were simultaneously exposed as shown in Fig. 1. Proton recoil tracks were counted on equal areas (of 2 cm^2) on each plate, these areas being situated at the same distance from the centre of the Be-piece. Only tracks having angles with the direction of the entering neutrons smaller than 45° were taken into account, assuming the shrinkage of the C2 emulsion to be 2.5. The figures obtained in two exposures lasting altogether 240 hours for all the elaborated areas were as follows: 2512 tracks in the 1-st group of the length of about 12μ and 307 tracks in the 2nd group of the length of about 22μ .

In order to evaluate the relative intensities of our lines or the ratio of the numbers of photons of the energies 3.20 MeV and 2.62 MeV emitted by the mesothorium source, the escape corrections which were different for each track length, the different cross-sections for scattering collisions of neutrons with protons, the different cross-sections for (γ, n) reaction in ^8Be for γ -ray energies 3.20 MeV and 2.62 MeV [7], and the different absorption coefficients in lead for these γ -ray energies, had all to be taken into account. The resulting figures for the intensity ratio of the line at 3.20 MeV and 2.62 MeV are of the order of 1:10 to 1:11. These figures indicate a considerably larger relative intensity of the line at 3.20 MeV than does the single previous result of Alichanov and Latyshev [3].

It is well known that about 70 per cent of the beta disintegration of ThC' is followed by two γ -rays of energy 0.58 MeV and 2.62 MeV. According to this ThD ($^{208}_{82}\text{Pb}$) must possess three energy states 0, 2.62 and 3.20 MeV. The spins of these states as theoretically calculated by Hulme [8] and Oppenheimer [9] are 0, 2 and 3 respectively; experimentally determined they are according to Martin and Richardson [10] 0, 1 and 3, and as found by Petch and Johns [11] 0, 2 and 4. In any case, owing to the large spin difference, the transition from the second excited state of ThD to the ground one is of a higher order of forbiddenness as compared with the transition from the first excited state and this is no doubt responsible for the smaller relative intensity of the γ -ray line at 3.20 MeV.

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The Application of the Antimony Microelectrode to Potentiometric Chromatography in Mixed Solvents of Benzine, Alcohol and Water

by

B. KAMIENSKI, K. PUCHAŁKA and Z. DOLIŃSKI

Communicated by B. KAMIENSKI at the meeting of May 18, 1953

When investigating non-conducting solutions by the method of potentiometric chromatography, it is necessary to prepare conducting films of silica gel on the ground surface of the microelement. This is superfluous in aqueous solutions. However, benzine-alcoholic solutions are often used in adsorption analysis, and it was interesting to ascertain whether the small quantities of water added to the benzine and ethyl alcohol were sufficient to build up the conditions necessary for the existence of hydrogen ions and, consequently, for the use of B. Kamiński's antimony electrode (see References at the end of this paper). The subject becomes still more interesting when we consider the possibility of so adapting the electrode that it may be used for making a volumetric analysis of the natural fatty acids which are analysed in benzine-alcoholic media. It often happens that these are dark, and so the application of indicators is difficult: the antimony electrode, however, may be used in coloured solutions.

The antimony electrode was put into a fatty acid solution of a concentration of approximately 0.01 M. Different alcohols were used as solvents, namely methyl, ethyl, propyl, buthyl alcohols (96% ethyl alcohol with 4% water). In the last experiment a mixture of 50% benzine with 48% alcohol and 2% water was applied as a solvent. The dissolved acids were titrated with a solution of 0.01 n potassium hydroxide, dissolved in one or other of the solvents, either an alcohol or the benzine-alcohol mixture. The results of the measurements of the potential of the antimony electrode against a 0.1 n calomel electrode are represented in Figs. 1, 2, 3, 4 and 5. Approximately the same volumes were used. Fig. 1 represents the titration of stearic acid in methyl alcohol, Fig. 2 — the titration of the same acid in propyl alcohol, Fig. 3 — the titration in buthyl alcohol, and Fig. 4 — in ethyl alcohol (with 4% water).

The last. Fig. 5, shows the result of titration when the above-mentioned mixture of benzene, alcohol and 2% water is applied as a solvent. A comparison of the figures shows clearly that the potential-change was

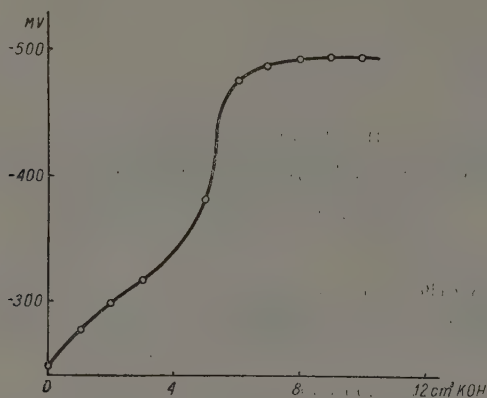


Fig. 1

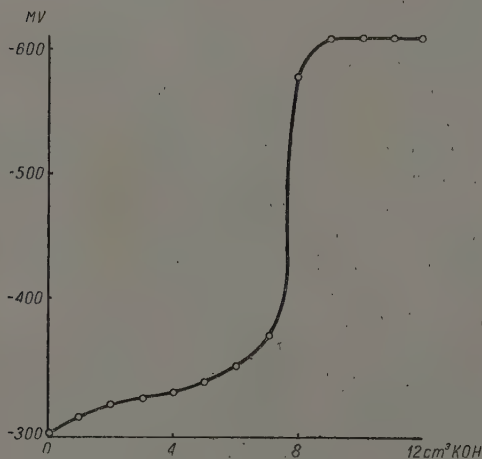


Fig. 2

greatest in the mixed solvent, and this fact is most interesting. The experiments convinced us that the application of different alcoholic solvents, and especially of a mixture, is quite possible because hydrogen ions are built in such solvents and the antimony electrode signals the presence of the ions sufficiently well.

Having noted these facts, we applied the mixed solvent and the antimony microelectrode in the method described in the papers cited (see References at the end of this paper). Silica gel produced in the U. S. S. R. was

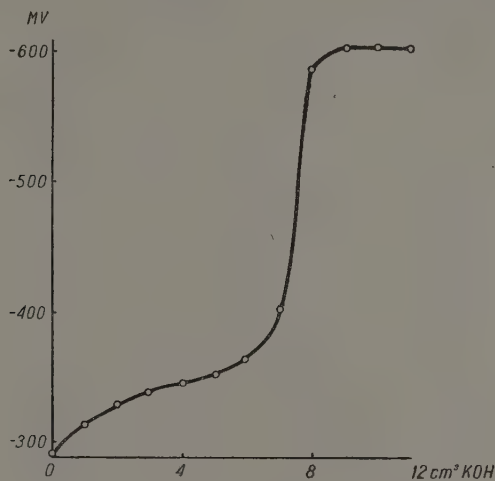


Fig. 3

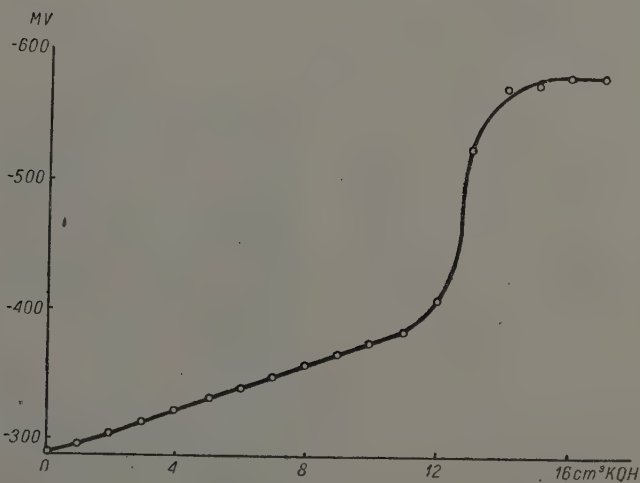


Fig. 4

used as an adsorbent. It was dried at a temperature of 105° C. A benzine-alcohol mixture containing 2% water was applied as a solvent and eluent. Stearic acid (chemically pure) produced in the U.S.S.R. and Merck's oleic acid were dissolved separately in the mixed solvent and in the 0.01 n solutions which had been prepared. 3 cm.³ of stearic acid solution were put

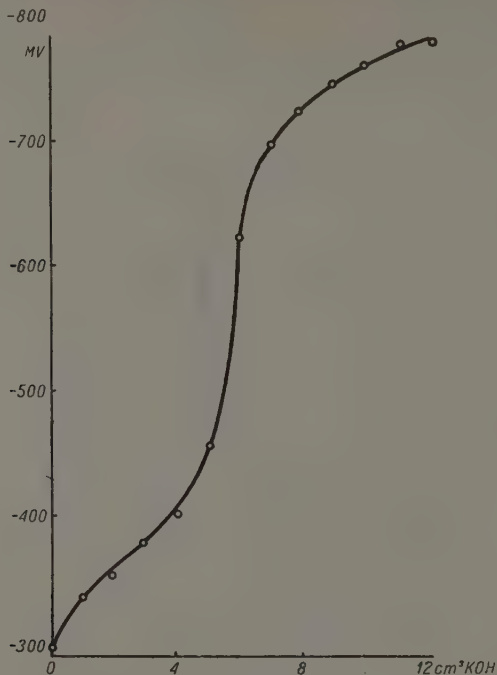


Fig. 5

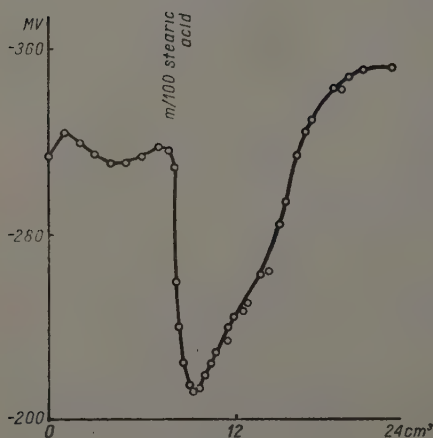


Fig. 6

on the top of the silica gel column which was 3 cm. high and 0.7 cm. in diameter. Fig. 6 shows the measurements of the electrode potential plotted against the volume of the eluent passing through the column. The experiment lasted 77 minutes. Oleic acid of similar concentration and under similar physico-chemical conditions gave the curve represented in Fig. 7. The experiment lasted 75 minutes. The actual moment of pouring the solution onto the top of the column is represented by an arrow.

The results show that diluted solutions cause quite marked changes in the potential and that the change in potential which accompanies the movement of the acid as it passes through the column can be easily observed.

The next step in the measurements was to apply a mixture of the two acids. 2 cm.³ of 0.01 n stearic acid and 2 cm.³ of oleic acid of the same concentration were mixed together and poured onto the top of the column. The experiment lasted 70 minutes; the result is represented in Fig. 8.

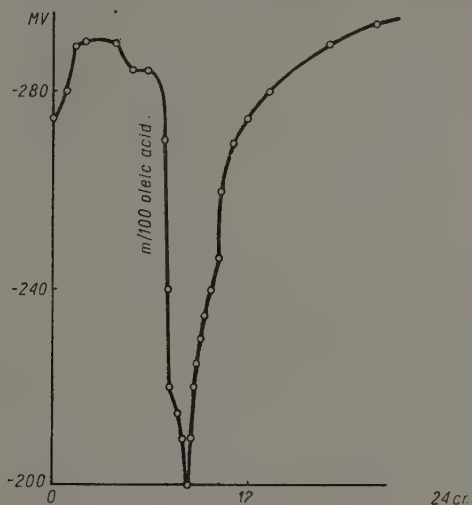


Fig. 7

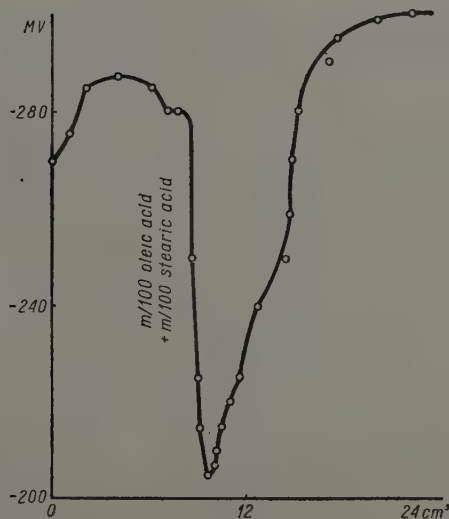


Fig. 8

No marked separation was visible, as may be seen from Fig. 8. From the point of view of potentiometric chromatography one would expect that the more dilute solutions of the mixtures would separate more readily.

Even very dilute solutions of weak acids are signalized by the antimony microelectrode, and so a mixture of 2 cm.³ of 0.002 n of each acid (stearic and oleic) was placed on the top of the column and eluted with the mixed eluent. The experiment lasted 100 minutes. A partial separation

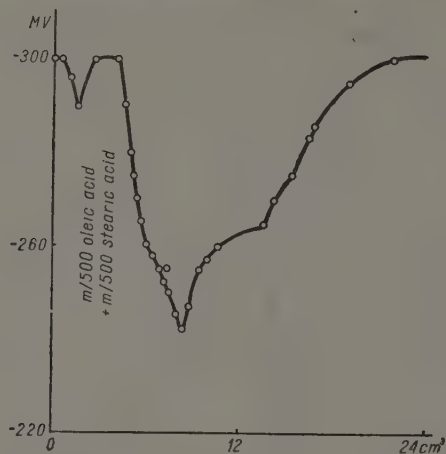


Fig. 9

can be observed in Fig. 9, which represents the results of the measurements. A further dilution was necessary to separate the acids more efficiently. Fig. 10 represents the results of a marked separation of stearic and

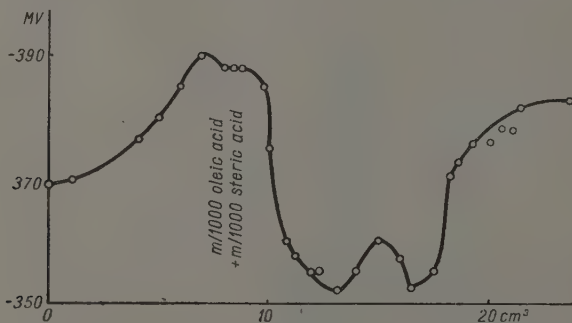


Fig. 10

oleic acid when 2 cm.³ of an 0.001 n solution were mixed with 2 cm.³ of an oleic acid solution of similar concentration and eluted after having been placed on the top of the column. The experiment lasted 70 minutes. Two minima, marking the separation of the acids, are visible in Fig. 10.

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The Separation of Atropine and Hyoscyamine by the Potentiometric Chromatographic Method

by

B. KAMIENSKI and K. PUCHAŁKA

Communicated by B. KAMIENSKI at the meeting of May 18, 1953

Atropine and, to a certain extent, also hyoscyamine are found in some plants indigenous to Poland, such as for instance, the deadly nightshade (*Atropa Belladonna*) and *Datura Stramonium*.

We were interested to see if it was possible to separate the racemic form (atropine) from active 1-hyoscyamine by means of selective adsorption and by observing the potential of an antimony microelectrode applied to the drops flowing out of an adsorption tube.

Alcoholic extracts were prepared from the leaves of *Datura Stramonium* and the roots of *Atropa Belladonna*, according to the method prescribed in the Polish Pharmacopoeia II. 1 kg. of liquor was extracted from 100 g. of leaves and roots. Assuming the plants to contain 0.3% of alkaloids, it was possible to reckon the concentration of alkaloids as being approximately 0.001 M. The solution was diluted, but dilute solutions are suitable for potentiometric chromatography. The solutions were analysed on aluminium oxide columns. Changes in the potential were measured in the usual way by putting an antimony microelectrode into the drops flowing out of the adsorption tube and applying a Lindemann electrometer, supplied by the Cambridge Instrument Company. In the last experiment a mixed solvent, viz. benzine, alcohol and water, was used. The preceding paper, "The Application of an Antimony Microelectrode to Potentiometric Chromatography in Mixed Solvents of Benzine, Alcohol and Water" by B. Kamiński, K. Puchałka and Z. Doliński, explains the use of the electrode in non-aqueous solutions. It contains also all the necessary references and so no references are given in this paper.

The respective solutions were put on top of an aluminium oxide column. The volume of each solution used for this purpose was 4 cm³. Two preparations of aluminium oxide were applied: E. Merck's aluminium oxide and Brockmann's oxide prepared for chromatographic purposes. On account

of the fact that the latter contained various alkalis, it had to be thoroughly washed. The washing lasted 45 days, and 75 litres of distilled water were used to purify 250 g. of aluminium oxide. The height of the column was 10 cm. and the diameter 0.7 cm. Alcohol (60 and 80%) was used as an eluent. In the last experiment, however, where the best separation of the racemic and optically active compound was obtained, a mixture of benzene and alcohol was used.

The diagram in Fig. 1 represents an incomplete separation of the alkaloids extracted from leaves of *Atropa Belladonna* on E. Merck's aluminium oxide. The elution lasted 100 minutes.

The same experiment carried out on eluted aluminium oxide lasted 155 minutes and the diagram in Fig. 2 represents the potential of the electrode plotted against the volume of the eluent flowing out of the adsorption tube. The numbers

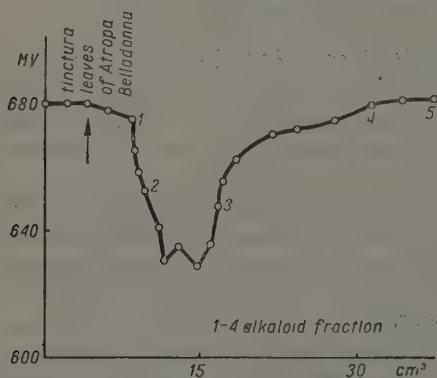
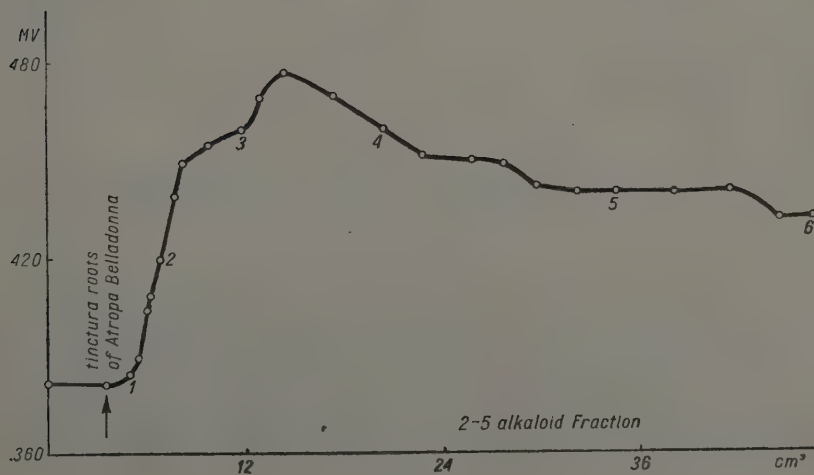
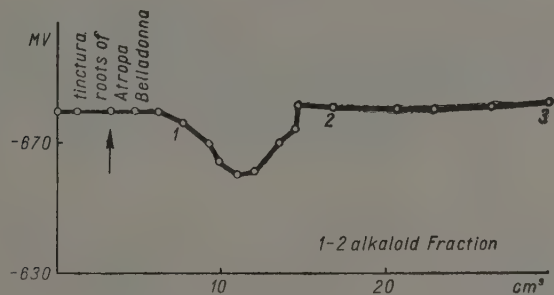
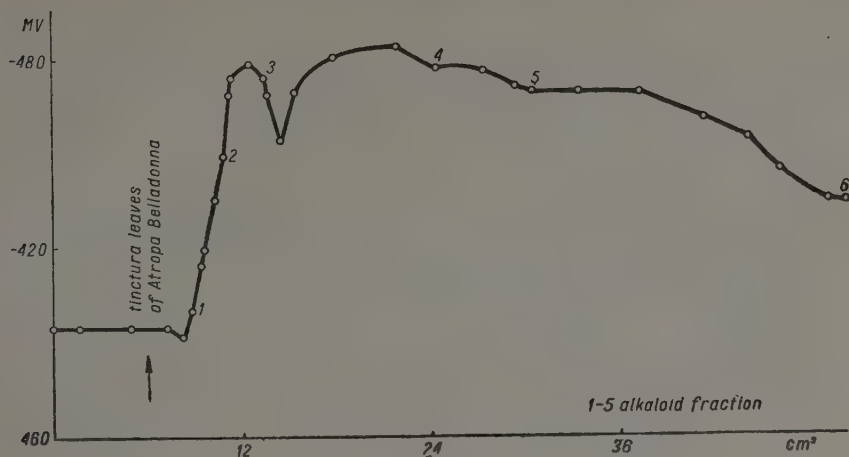


Fig. 1

drawn along the curve show the fractions which gave a characteristic fluorescence in ultraviolet light. The arrow marks the actual moment of pouring the alkaloid solution on top of the column. A comparison of the diagrams (Figs. 1 and 2) shows that the initial potential of the electrode depends on the origin of the aluminium oxide preparation. The washed preparation was neutral, Merck's aluminium oxide was alkaline. The eluent flowing through the oxide became alkaline and on account of this the buffer capacity of the alkaloids flowing out of the column decreased the alkalinity. When the eluent was neutral, after flowing through the thoroughly-washed oxide, the amphoteric alkaloids showed their true fundamental character. In the first case a minimum of the potential (Fig. 1) appeared, in the last, a maximum was visible (Fig. 2). An extract obtained from the roots of the same plant exhibited similar behaviour on the part of the potential, thus signaling the presence of alkaloids. The potential depended on the reaction of the adsorbent. Figs. 3 and 4 represent the plots of the potential. Experiment 3 lasted 72 minutes, experiment 4—128 min.

Similar observations were made in the case of extracts of *Datura Stramonium* leaves, as may be gathered from Figs. 5 and 6. The alkaline aluminium oxide of E. Merck was used in the fifth experiment (Fig. 5) and eluted oxide in the sixth (Fig. 6). Experiment number five lasted 127 minutes, number 6 — 146 minutes.

The curves representing the change of the potential against the volume flowing out of the column differ fundamentally in character. The diffe-



rence depends on the degree of alkalinity of the adsorbent. When the adsorbent is basic (E. Merck's unwashed preparation), the initial potential of the antimony electrode is rather negative against a 1/10 n calomel electrode and amounts to approximately -680 mV. When the preparation was washed

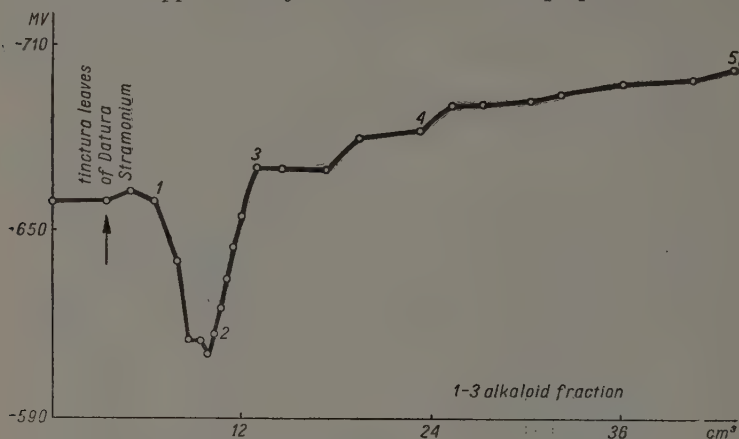


Fig. 5

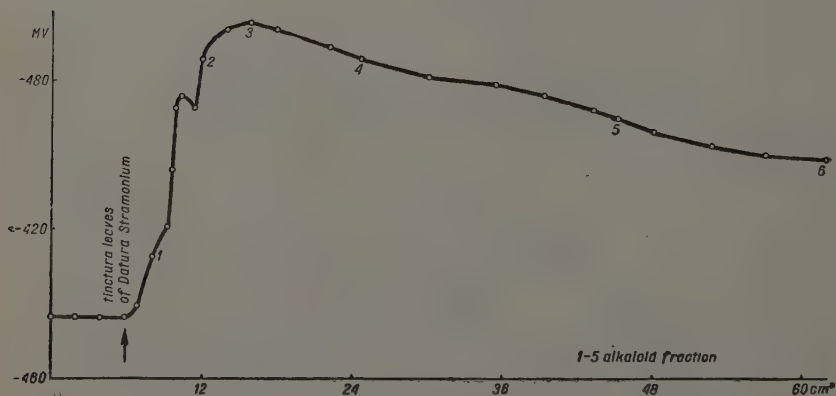


Fig. 6

thoroughly the potential was less negative and amounted approximately to -400 mV. The change in potential during the analysis signalizes the presence of alkaloids by a maximum or a minimum. The fractions of the elute associated with the maximum or minimum were tested chemically, optically and electro-chemically. Vitali's chemical test was applied. A volume of some cubic centimeters of different fractions was treated with some

drops of concentrated nitric acid, evaporated on a water bath and alkalinized with some drops of an alcoholic solution of potassium hydroxide. A violet-red tint appeared when the alkaloids were present. The fluorescence of the alkaloids is much more selective in ultraviolet light. Atropine shows a bluish-white and hyoscyamine a reddish-violet fluorescence. When extracts of *Atropa Belladonna* were analysed the fluorescence of hyoscyamine was very slight. Extracts of *Atropa Belladonna* roots did not appear to contain hyoscyamine. The leaves contained very little. A much stronger fluorescence was produced by the analysed extracts of *Datura Stramonium* leaves. In the fifth experiment ultraviolet light was applied and the fluorescence of the elution flowing out of the adsorption tube was observed; it was noticed that hyoscyamine appeared first and that it was present in appreciable quantities in the extract of *Datura Stramonium* leaves. The alkaloid fraction determined by the potential (approximately 6.6 cm.³) was collected separately and analysed for the second time on a higher column of Merck's aluminium oxide (20 cm. high). The solvent, however, was prepared in such a manner that its composition was 77% ethyl alcohol, 14.5% benzine, 8.5% water. The water content can be explained by the fact that 60% alcohol was used in extracting the leaves. Atropine and hyoscyamine differ as regards their solubility in benzine and the presence of 14.5% of benzine was enough to change the conditions appreciably.

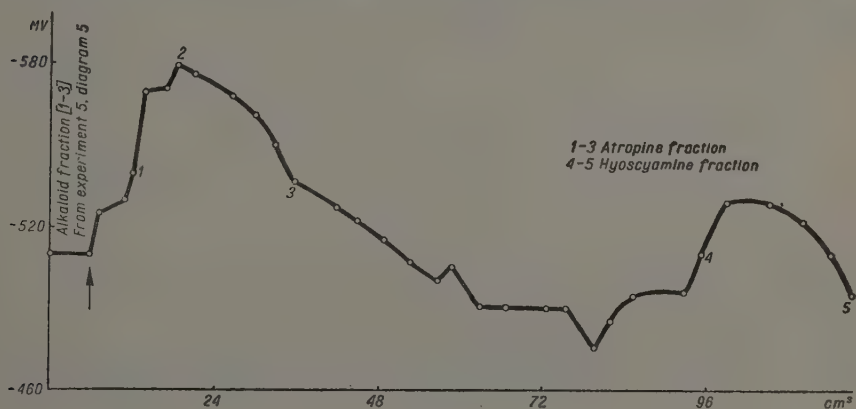


Fig. 7

Figure 7 represents the potential of the antimony electrode against the volume of the solvent flowing out of the 20 cm. high adsorption column. The numbers along the curve mark the fluorescence of atropine or of hyoscyamine. Atropine appeared first in the elution and after 100 minutes the fluorescence of hyoscyamine became clearly visible. The whole experiment lasted 307 minutes. The order of appearance of the two forms was reversed when the alcoholic solvent was used. The separation of both forms was excellent.

The Mechanism of Reduction of KMnO_4 by concentrated KOH Solution

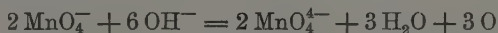
by

B. JEŻOWSKA-TRZEBIATOWSKA, J. NAWOJSKA and M. WRÓŃSKA

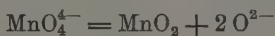
Communicated by W. TRZEBIATOWSKI at the meeting of January 12, 1953

In previous experiments [1] we found that the spontaneous reduction of KMnO_4 in concentrated alkaline solution leads to the stepwise reduction of manganese through Mn^{VI} and Mn^{V} to Mn^{IV} . In this process the colour of the KOH solution changes from violet through green to blue and there remains a colourless solution after MnO_2 has been completely precipitated. Mn^{VI} can be isolated as BaMnO_4 [2], Mn^{V} as $\text{Na}_3\text{MnO}_4 \cdot 10\text{H}_2\text{O}$ at low temperatures.

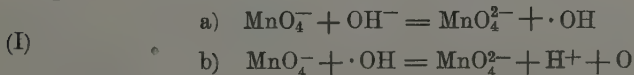
In the total absence of reducing agents in alkaline solutions of permanganate, the hydroxyl ion itself acts as electron donor. This is expressed by the following reaction:



The unstable ion MnO_4^{4-} is at once converted:



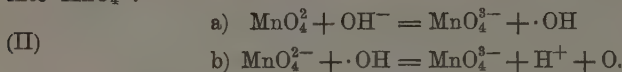
Our work has shown that the above equation represents the reaction only summarily. The mechanism of the reaction is, in fact, extremely complicated, and its rate depends to a large extent on the activity of the alkali. In the first stage of the reaction, MnO_4^{2-} ions are formed at a practically infinitely high velocity, owing to the particular ability of MnO_4^- to act as an electron acceptor.



In this reaction some $\cdot\text{OH}$ radicals are an intermediary form and are capable of further reducing the MnO_4^- ions either directly as H_2O_2 ($2\cdot\text{OH} = \text{H}_2\text{O}_2$) or through decomposition according to $2\cdot\text{OH} = \text{H}_2\text{O} + \text{O}$.

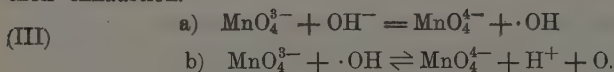
Direct experiments have confirmed that an alkaline solution of permanganate is at the same time a very dilute solution of $\cdot\text{OH}$ radicals [6].

In the second stage of the reduction the MnO_4^{2-} ions are converted into MnO_4^{3-} .



The MnO_4^{2-} ion is a weaker acceptor of electrons due to its greater negative charge. For this reason the reaction rate decreases after MnO_4^- disappears from the solution.

The third stage of the reduction in concentrated KOH consists in the final change of MnO_4^{3-} into MnO_2 at a very low rate, which is a proof of the modified character of the process. The considerable negative charge of the ion renders the reduction of an OH^- ion (II)a) unlikely, and its rate must in any event be close to zero. The function of reducing agents can be partly fulfilled by H_2O_2 or the $\cdot\text{OH}$ radicals, formed in the preceding reactions. This is probably why the reduction rate decreases sharply after their exhaustion.



We have found an increase in the reduction rate under the influence of light, especially ultra-violet radiation, in the reaction: $\text{MnO}_4^{3-} \rightarrow \text{MnO}_2$. The radiation absorbed by OH^- ions (maximum of absorption 1800–2000 Å) accelerates the transfer of the electron to the neighbouring ions [3] and in these may accelerate reaction (III).

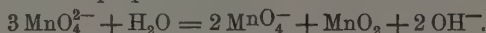
The experiments have shown that oxygen has an inhibitory effect on the reduction rate of MnO_4^{3-} and must therefore exert some influence in establishing the equilibrium of reversible reaction (III)b).

In solutions of moderate KOH concentration (about 1 M) the MnO_4^{3-} ion is converted by the process:



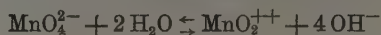
The equilibrium of this reaction is shifted to the left in concentrated KOH solutions.

In dilute solutions of KOH ($< 0.001 \text{ M}$) the reduction rate is very low and the MnO_4^{2-} ion also disproportionates:



In the first case the solution remains green until the end of the reaction; in the second case it remains violet. It is possible that these reactions hold also in concentrated KOH. The only acceptor of the electron would then be the MnO_4^- ion, whose reduction rate exceeds that of the disproportionation reaction.

In order to explain the reduction of KMnO_4 by OH^- ions, it might be assumed that the MnO_4^{2-} ion dissociates as follows:



and that the newly formed MnO_2^{2+} continues to discharge until it is transformed into MnO_2 . In concentrated KOH solution the equilibrium of this reaction is shifted towards the left. Abel [4] accepted the existence of such ions but there is a lack of experimental proof in this respect. Furthermore, a reduction of cations does not account for the sudden change in the rate of the reaction.

Experimental part

For investigating the reduction rate, we used 25 ml. portions of $7.7 \cdot 10^{-3}$ M KMnO_4 in strong KOH solution (0.9–13.8 M). The measurements were made at $18^\circ \pm 0.1^\circ \text{C}$. The progress of the reduction of manganese was determined by titrating with 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ of the iodine in acid medium.

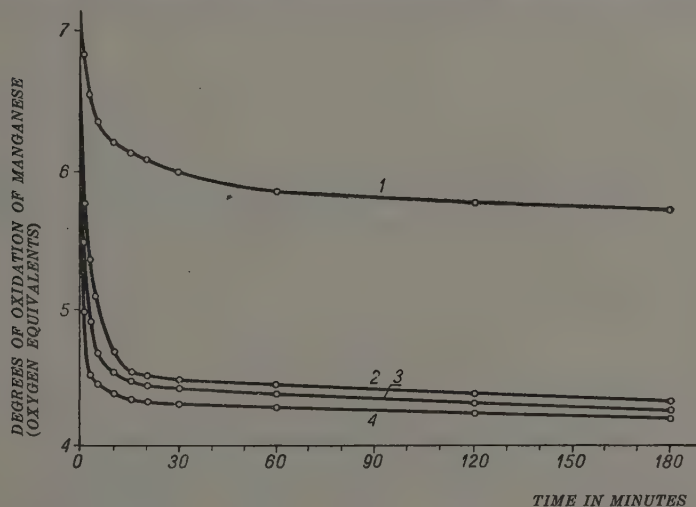


Fig. 1

- 1 — Reduction curve in 0.9 M KOH .
- 2 — Reduction curve in 6.2 M KOH .
- 3 — Reduction curve in 10.0 M KOH .
- 4 — Reduction curve in 13.8 M KOH .

The initial reduction rate which is, practically, $v=\infty$, decreases to $v=c$ after the disappearance of MnO_4^- and then, within the range of the third oxygen equivalent, to nearly $v=0$ (Fig. 1). All the manganese is transformed into MnO_2 after ten hours in 13.8 M KOH and after sixteen hours in 6.8 M KOH . The curve then crosses the abscissa. Fig. 1 shows also the decreasing reaction rate as function of the KOH concentration. This is shown most distinctly in an 0.9 M solution, where the initial appreciable reaction rate has already decreased within the range of the second equivalent, the process of reduction being completed after some days.

The initial rate of reduction of permanganates was often explained by the reducing action of small quantities of organic substances [5]. In order to eliminate them, the solutions were prepared with water, double-distilled in the presence of KMnO_4 , boiled and cooled in a stream of N_2 . Solutions of KOH , first treated with KMnO_4 , were also used, until fully reduced to MnO_2 . The changes of oxidation states of manganese were the same as in the untreated KOH solution.

It was assumed that the process of spontaneous reduction of KMnO_4 is caused by peroxides formed under the action of atmospheric oxygen [5], [6]. In order to examine the dependence of the reduction on oxygen content, experiments were made in an oxygen and also in a nitrogen atmosphere which at the same time eliminated the oxygen produced in the reaction (Fig. 2).

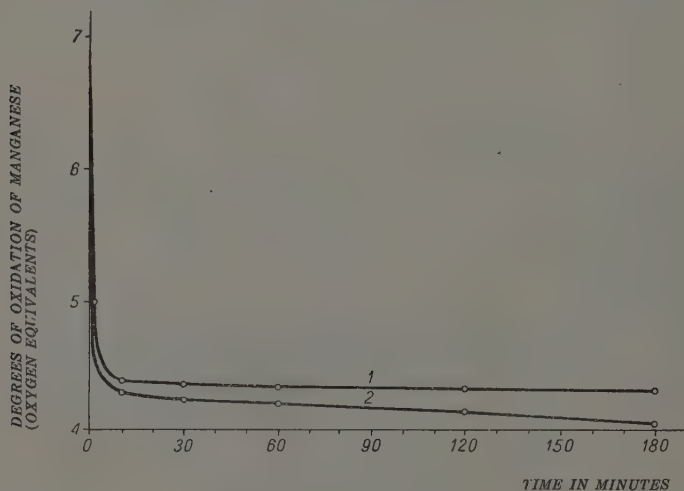


Fig. 2

- 1 — Reduction curve in oxygen atmosphere.
2 — Reduction curve in nitrogen atmosphere.

In the nitrogen atmosphere there is an increase in the reaction rate within the range of the third equivalent. On the other hand in an oxygen atmosphere there is a marked slowing down of the process.

Measurements of reaction rates in darkness, in daylight, and under mercury lamp radiation have shown that the reaction is accelerated by light (Fig. 3, curves 2 and 3), but that the latter influence is not essential (curve 1).

The general aspect of the curves remained unchanged. The increase of the reduction rate is observed in particular during the third stage within the range of the third equivalent ($\text{Mn}^{\text{V}} \rightarrow \text{Mn}^{\text{IV}}$).

Attempts to show the presence of radicals in the alkaline solution of KMnO_4 were successful. The $\cdot\text{OH}$ radicals react with benzene or its derivatives [7] according to:

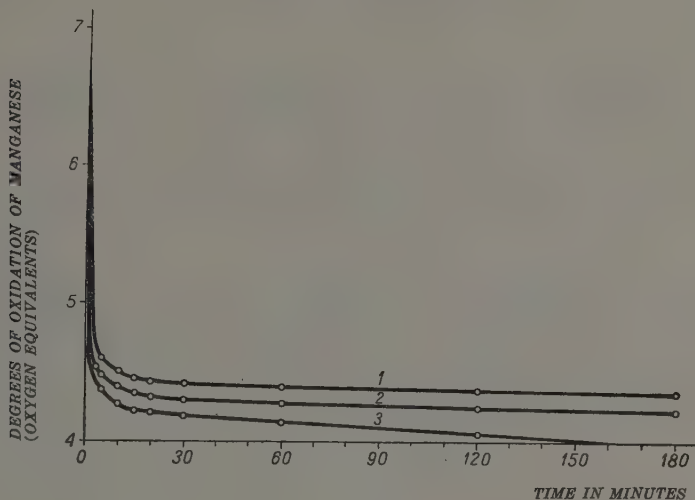
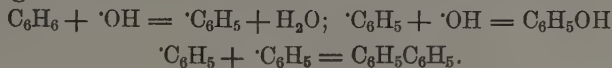


Fig. 3

- 1 — Reduction curve in darkness.
- 2 — Reduction curve in daylight.
- 3 — Reduction curve under mercury lamplight.

An alkaline permanganate solution (13.8 M KOH , 10^{-2} M KMnO_4) was thoroughly mixed with benzene, purified by repeated freezing and several hours mixing with KMnO_4 . After separating the benzene and filtering of the MnO_2 , the presence of phenol in the aqueous solution was confirmed. In the presence of an excess of KMnO_4 , it was found that the alkaline solution contained oxidation products of phenol such as tartaric acid and oxalic acid. These were identified microscopically and by special reactions. From the benzene solution diphenyl was also isolated.

Department of Inorganic Chemistry, Institute of Technology, Wrocław

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Magnetic Susceptibilities of Niobium Hydrides

by

W. TRZEBIATOWSKI and B. STALIŃSKI

Communicated by W. TRZEBIATOWSKI at the meeting of May 18, 1953

Metallic niobium dissolves large quantities of hydrogen thereby forming a new regular body-centered hydride phase (β), which was formulated by J. Umanski [1] as NbH. Dissolved hydrogen only slightly expands the lattice of niobium [2] and the β -phase represents the same, only more expanded, type of metallic lattice. A. Sieverts and H. Moritz [3] have shown, from hydrogen isobars, that the heterogeneous range of the metal and hydride phase extends from NbH_{0.08} to NbH_{0.66}.

For the purpose of these investigations a series of 9 niobium hydrides was prepared in the same manner as previously described [4]. Spectroscopic pure niobium metal powder (Johnson Matthey), showing only faintly visible lines of aluminium, was used. With a large excess of hydrogen, compositions up to NbH_{0.86} were obtained, showing at this composition a hydrogen evolution in vacuum already at room temperature.

Fig. 1 shows the results of X-ray analysis by powder diagrams after Debye-Scherrer-Hull and Preston. Metallic niobium dissolves hydrogen up to NbH_{0.10} and causes a lattice expansion from $a = 3.303 \text{ \AA}$ to $3.318 \text{ \AA}$. The heterogeneous region of the $\alpha + \beta$ -phase extends from NbH_{0.10} to NbH_{0.57}. In this region the β -phase has a lattice constant of $3.405 \text{ \AA}$, but with a higher hydrogen content the lattice constant rises to $3.442 \text{ \AA}$ at NbH_{0.86}.

The results, using the Gouy method of measuring magnetic susceptibility between 80°K and 290°K are plotted in Fig. 2. The susceptibility of very pure niobium amounts to $\chi_g = 2.17 \pm 0.02 \cdot 10^{-8}$ at 292°K with

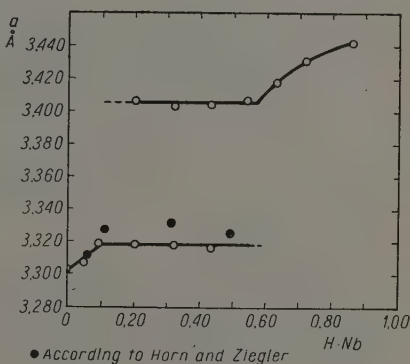


Fig. 1

a negative temperature coefficient: $\chi_g = +2.22 \cdot 10^{-6}$ at 80°K and $\chi_g = +2.12 \cdot 10^{-6}$ at 470°K . This result differs only slightly from $\chi_{289^\circ} = +2.28 \cdot 10^{-6}$, as previously determined by W. J. de Haas and P. M. van Alphen [5].

Upon introducing increased amounts of hydrogen, one observes that the susceptibility of niobium gradually diminishes. The negative temperature

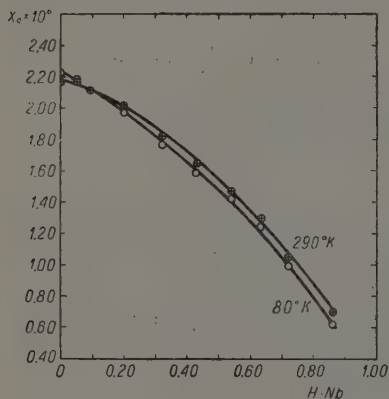


Fig. 2

coefficient of metallic niobium varies, so that at $\text{NbH}_{0.09}$ susceptibility is independent of temperature and with a higher hydrogen content the temperature coefficient is positive, but susceptibility still diminishes. For $\text{NbH}_{0.86}$ $\chi_g = +0.62 \cdot 10^{-6}$ at 81°K and $\chi_g = +0.70 \cdot 10^{-6}$ at 291°K .

The susceptibility isotherms of niobium hydrides closely resemble the susceptibility isotherms of the palladium-hydrogen system [6], although the electronic structure of niobium differs from that of palladium. Palladium finishes the filling of d shells, where probably 0.6 vacant place/atom exist. Niobium has less than the half of d shells occupied. Therefore, assuming that dissolved hydrogen

is ionised, it seems that the diminished paramagnetism of niobium hydrides may originate from such a strong coupling of d shells, that the effective magnetic moment of the niobium core diminishes in spite of the increased number of electrons. According to the theory of C. Zener [7] concerning metals of the V subgroup such strong coupling is to be expected.

Department of Inorganic Chemistry, Institute of Technology, Wrocław

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On Certain Hydroxamic Acids as Antitubercular Agents

by

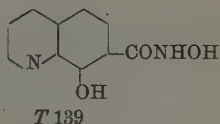
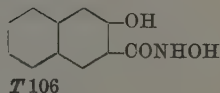
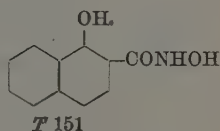
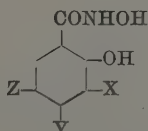
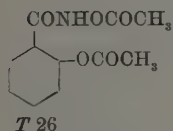
T. URBĄŃSKI

Communicated at the meeting of June 22, 1953

In 1948 the author suggested using salicylhydroxamic acids as an anti-tubercular agent "T 2". The first results *in vitro* and *in vivo* were published between 1949—50 [1]. The substance showed promising results when subjected to clinical examination by S. Hornung in fifteen cases of pulmonary tuberculosis [2]. The substance was well tolerated by the patients, when large doses of 10—20 g./day were administered.

This led the author of the present paper to look for more potent derivatives of salicylhydroxamic acid or for analogous substances. Eventually, a number of hydroxamic acids, most of them as yet unknown in scientific literature, were prepared by a number of colleagues [3], [4], [5], [6].

The following were the new substances thus prepared:



T 95	X = CH ₃ ,	Y = Z = H
T 97	Y = CH ₃ ,	X = Z = H
T 100	Z = CH ₃ ,	X = Y = H
T 112	X = Z = CH ₃ ,	Y = H
T 143	X = OCH ₃ ,	Y = Z = H
T 40	Z = Br,	X = Y = H
T 181	X = Z = Br,	Y = H

The substances T 95, T 97, T 100, T 112, T 143, T 151, T 106, T 139 were obtained in the conventional way by the action of hydroxylamine on the methyl esters of the corresponding carboxylic acids [3].

T 26 was formed by the acetylation of *T* 2 with acetic anhydride. *T* 40 was originally prepared by T. Urbański and Lewenstein by direct bromination of salicylhydroxamic acid in an acetic acid medium [4]. Later on, Eckstein improved the method by treating methyl 5-bromosalicylate with hydroxylamine in an alcoholic solution [5]. He also prepared a dibromo-derivative (*T* 181) by treating methyl 3,5-dibromosalicylate with a hydroxylamine solution as above.

Some of the known hydroxamic acids, such as: 4-hydroxybenzohydroxamic acid — "*T* 145" — and oleilhydroxamic acid ("*T* 173"), and some new hydroxamic derivatives of the cholic acids: "*T* 183" and "*T* 184" [6] were also prepared and examined.

Their bacteriostatic concentrations against saprophytic mycobacteria determined *in vitro* by S. Ślopek are tabulated below (Table I).

TABLE I

Substance	N a m e	Melting point °C.	Bacteriostatic concentrations mgm. per 100 ml. of Sodium salts.
<i>T</i> 2	Salicylhydroxamic acid	168 decomp.	5—60
<i>T</i> 26	Diacetylsalicylhydroxamic acid [4]	130	126—250
<i>T</i> 95	3-Methyl-salicylhydroxamic acid [3]	149—150 dec.	15—75
<i>T</i> 97	4-Methyl-salicylhydroxamic acid [3]	190—192 „	62.5—125
<i>T</i> 100	5-Methyl-salicylhydroxamic acid [3]	185	62.5—125
<i>T</i> 112	3,5-Dimethyl-salicylhydroxamic acid [3]	154—156	7.5—15
<i>T</i> 143	3-Methoxysalicylhydroxamic acid [3]	144	inactive
<i>T</i> 40	* 5-Bromosalicylhydroxamic acid [4]	232 decomp.	15—30
<i>T</i> 181	3,5-Dibromosalicylhydroxamic acid [5]	182—183 dec.	62—125
<i>T</i> 151	1-Hydroxynaphto-2-hydroxamic acid [3]	168 decomp.	31.2
<i>T</i> 106	2-Hydroxynaphto-3-hydroxamic acid [3]	191—192 „	8—16
<i>T</i> 139	8-Hydroxyquinoline-7-hydroxamic acid [3]	208—209 „	2—4
<i>T</i> 145	4-Hydroxybenzoxamic acid	174 decomp.	31
<i>T</i> 173	Oleilhydroxamic acid Sodium Salt	—	inactive
<i>T</i> 183	Cholohydroxamic acid [6]	150	250—500
<i>T</i> 184	Desoxycholohydroxamic acid [6]	168	125

The sodium salts of the products *T* 2, *T* 95, *T* 112, *T* 40, *T* 106, *T* 139 were examined by J. Venulet from the point of view of their toxicity to rats. The lethal doses expressed in g. per kg. of body-weight are shown in Table II.

It is of interest to note that the toxicity of the hydroxamic acids is very slight when taken *per os*, being much higher when administered by injection. This suggests that either the substances, when taken *per os*, are transformed into less toxic products, or that particularly when injected intravenously they are transformed into more toxic products.

TABLE II

	Lethal doses (g./kg. body weight)		
	<i>per os</i>	Subcutaneous	Intravenous
<i>T</i> 2	—	1.4	—
<i>T</i> 95	ca. 3.0	0.6	0.15
<i>T</i> 112	ca. 3.0	—	—
<i>T</i> 40	ca. 3.5	0.8	0.12
<i>T</i> 106	ca. 2.0	*)	*)
<i>T</i> 139	ca. 2.0	0.3	0.03

Experiments *in vivo* were carried out by S. Šlopek with the substances *T* 2 [1], *T* 95, *T* 40, *T* 106 [7]. Guinea pigs (ca. 500 g.) were inoculated intraperitoneally with 0.1 mg. of *Mycobacterium tuberculosis*, *H*₃₇ *Rv* strain. Administration of the drug was begun on the eighth day after inoculation and was continued for forty-two days. Thirty-five days later the animals were killed and the extent of the tuberculosis was examined. The results are shown in Table III.

TABLE III

Substance	Animals (their number)	Daily dose mg. per animal	Administration	Mortality %	Average tuberc. index	Average survival time (days)
<i>T</i> 95	20	10	Subcutaneous	50	73	
<i>T</i> 40	20	10	"	20	65	80.2
<i>T</i> 106	20	10	"	30	70	
Strepto-mycin	20	10	"	10	57	84.4
Controls	20	—	—	90	100	47.2

The experiments *in vivo* with salicylhydroxamic acid (*T* 2) were repeated by Gardner, Wenis and Smith [8]. They did not find any antitubercular activity in mice. This may be due to the following fact observed by Šlopek [9] with regard to *T* 40: he found that only when mice were subjected to a chronic form of T. B., was *T* 40 effective as an antitubercular agent, but that it was ineffective when the form of the disease was acute.

*) Has not been determined because of its low solubility in water.

The product *T* 40 was selected for clinical examination. Over 220 cases of T. B. reacted favourably to the product. Part of the results have already been described [2] and the rest will be reported elsewhere [10], [11], [12], [13], [14]. Particularly interesting are the cases of tubercular meningitis which have not been influenced by streptomycin and *iso*-nicotinoylhydrazine. In many cases an additional administration of *T* 40 resulted in a considerable improvement [2], [10], [11].

The author's idea of using salicylhydroxamic acid was originally based on the assumption that it would combine the curative properties of some salicylic acid derivatives with those of certain amino compounds as the hydroxamic group can be considered as a potential amino-group. Indeed it has been found by Turski [15] and confirmed by the author [16] that hydroxamic acids can be used as aminating agents.

Recently, Eckstein [5] expressed the view that hydroxamic acids may be subjected to the Lossen rearrangement in the living organism. Thus, salicylhydroxamic acid would be transformed into *o*-aminophenol or benzoxazolone. (The antitubercular properties of *o*-aminophenol are known [17]). It is worth pointing out that a number of derivatives of hydroxylamine have been found among natural products, e. g. the amino-acid, canavanine, has been isolated from soya bean meal [18].

Virtanen et al. [19] found that oxymes are formed in aerobic cultures of *Azotobacter* or *Clostridium butyricum*. Two cyclic hydroxamic acids are known: aspergillie acid produced by *Aspergillus flavus* [20], and nocardamine, produced by *Nocardia* (*Actinomycetaceae Buchanan*) [21].

It has also been demonstrated by Slavik [22] that hydroxamic acids can be formed from some amides and peptides, through their enzymatic oxidation in the kidneys of rats.

It has also been shown that hydroxamic acids can be formed from acids and hydroxylamine through the action of enzymes [23].

All these results seem to indicate the importance of hydroxamic acids in the metabolic processes.

The author is much indebted to Prof. S. Ślopek for carrying out the *in vitro* and *in vivo* experiments and to Dr J. Venulet, for examining the toxicity of the substances.

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On the Antitubercular Properties of 5-Bromosalicylhydroxamic Acid (»T 40«)

by

S. ŚLOPEK

Communicated by T. URBĄŃSKI at the meeting of June 22, 1953

Continuing the line of research (originally suggested by T. Urbański) into the antitubercular properties of salicylhydroxamic acid and its derivatives, a new series of tests *in vitro* and *in vivo* have been carried out with 5-bromosalicylhydroxamic acid (»T 40«).

It has been found *in vitro* on Youmans medium, that T 40 is much more effective against virulent strains of *Mycobacterium tuberculosis* than against saprophytic mycobacteria (Table I).

TABLE I

<i>Mycobacterium tuberculosis</i>	Minimal inhibiting concentration
(<i>t. humanus</i> — $H_{37}Rv$)	75 mcg./ml.
(<i>t. bovinus</i> — Ravenel)	75 mcg./ml.
(B C G)	150 mcg./ml.
(<i>t. apium</i>)	660 mcg./ml.
Saprophytic mycobacteria	
(6 strains)	150—600 mcg./ml.

A striking difference was found *in vivo* depending on whether the experimental tuberculosis of animals had an acute or chronic form. It has been found now that »T 40« is not active against an acute form of experimental tuberculosis. On the other hand, »T 40« is strongly active against a chronic form of experimental tuberculosis in guinea pigs.

The results are to be seen in Table II. In the top part are shown the results in the case of acute T.B. Below are shown the results in the case of chronic T.B.

We are inclined to think that this observation explains the difference between our results and those of Gardner, Wenis and Smith [2], who did not find any activity of salicylhydroxamic acid in mice.

TABLE II

Substance	Daily dose mg./kg. (sub- cutaneous)	Number of animals	Observation time (days)	Average survival time (days)	Mortality	Average T. B. index
•T 40•	30	20	28	16.7	20/20	70
Streptomycin	30	20	28	20.0	0/20	49
Control	—	40	28	22.4	40/40	100
•T 40•	30	20	85	80.2	4/20	65
Streptomycin	30	20	85	84.4	2/20	57
Control	—	20	85	47.2	19/20	100

Silesian Medical Academy,
Institute of Tuberculosis, Warsaw.

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The Mechanism of Diffusion of Cathodic Hydrogen into Iron

by

M. ŚMIAŁOWSKI and Z. SZKLARSKA-ŚMIAŁOWSKA

Communicated by M. ŚMIAŁOWSKI at the meeting of May 18, 1953

It was stated in a previous paper [1] that a convenient method for the study of hydrogen penetration into iron consisted in measuring the linear expansion of the fine wire used as a cathode during the electrolysis of aqueous solutions of acids or alkalis. The experiments which we carried out using this method enabled us to obtain valuable information concerning the probable mechanism of this process.

In our study we used a mild steel wire with a diameter of 0.45 mm. The analysis of the wire was as follows:

C	Mn	Si	P	S	Cu	Ni	Cr	Fe
0.09	0.35	0.00	0.028	0.048	0.47	0.03	0.00	the remainder up to 100%

The apparatus was similar to the one used in our previous work [1]. The length of the wire acting as cathode in contact with the electrolyte was 180 mm. Mechanical-optical magnification enabled us to observe changes in length with an accuracy of 0.001 mm. A 200 g. weight served as a charge to extend the wire sample. The value of this charge which was examined within the limits of 100 to 500 g. had no effect on expansion so long as the tension was sufficient to overcome the friction taking place at the axle-bearing of the mechanical-optical lever. An anode, in the form of a spiral of platinum wire, surrounded the cathode, and both were immersed in 50 ccm. of solution. The lower end of the wire sample was fastened to an ungreased cut-glass stopper, which had a little glass hook. This stopper formed the bottom of the vessel in which the electrolysis took place.

As received, the wire had a high degree of strain-hardening produced by cold-work. The tensile strength of the wire was 95.1 kG per sq. mm. When the wire was in that state, hydrogenation caused only a very small degree of expansion. For the principal measurements the wire samples were annealed during 1 hour at different temperatures ranging from 400 to 900° C.

in a hydrogen atmosphere. Before each experiment the surface of the wire was carefully polished or etched by hydrochloric or nitric acids. After fastening the iron cathode, putting on the platinum anode and filling up the vessel (which was maintained at constant temperature) with solution, the electrolysing current was switched on. The elongation of the wire as a function of time was observed.

The majority of our experiments were carried out at 40°C. At that temperature all dimensional changes in the iron wire usually ceased 40 to 60 minutes after the commencement of electrolysis.

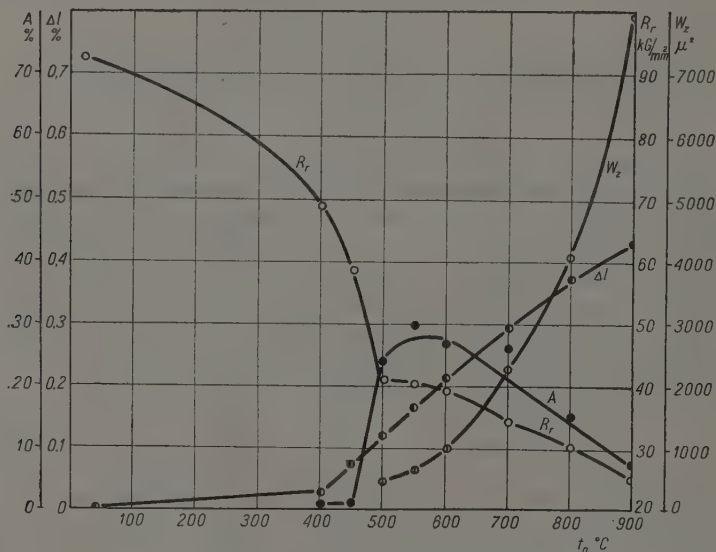


Fig. 1

The principal factors affecting the maximal expansion of a 0.45 mm. iron wire as a result of impregnation with hydrogen at 40°C. were found to be as follows:

1. The annealing temperature of the wire after cold-work.
2. The composition of the liquid from which the hydrogen was evolved.
3. The cathodic current density is smaller than about 0.1 amps. per sq. cm.

Fig. 1 shows the relationship between the annealing temperature (t_a , °C.) and the maximal elongation of the wire caused by saturation with hydrogen evolved at 40°C. and at a cathodic current density of 0.14 amps. per sq. cm. from a solution of 1 N H_2SO_4 , containing 0.15 g. thiourea per litre.

Each point on the Δl -curve represents an average value obtained from more than 10 determinations. In the same figure are plotted also the

values of the tensile strength (R_r , kG per sq. mm.), of the elongation to fracture (A , per cent) and of the grain size (W_z in sq. μ).

A comparison of the curves presented in Fig. 1 suggests that the degree of elongation of the iron wire, as a result of its saturation with cathodic hydrogen, depends on the following factors:

1. Tensile strength.

2. Grain size.

3. Decarburization of the steel when heated in hydrogen at 700 to 900°C.

The first-mentioned factor is probably the most influential.

Samples of the iron wire impregnated with cathodic hydrogen are very brittle and this brittleness does not wholly disappear upon removal of the hydrogen. For instance, the maximal number of bends that the wire can withstand without breaking is approximately as follows:

No	Condition	Number of bends
1	Annealed at 900°C.	~ 26
2	Treated in 1N H ₂ SO ₄ with thiourea (0.15 g. per litre)	~ 1
3	Treated in 1N H ₂ SO ₄	~ 5
4	Treated in 1N H ₂ SO ₄ with dibenzyl sulfoxide (0.1 g. per litre)	~ 9
5	Treated like No 2 and kept 2 days at room temperature	~ 4
6	Treated like No 2 and heated <i>in vacuo</i> for 30 minutes at 300°C.	~ 5

The volume of hydrogen extracted from samples Nos 2 to 4 by heating *in vacuo* was 0.5 to 1.1 cm. per 1 g. of iron. It was not easy to determine the exact value because of the rapidity with which the gas escapes from the metal even at room temperature and at normal pressure.

The expansion of the wire as a result of hydrogen impregnation was found to be entirely irreversible. The wire does not contract when the hydrogen is removed.

Fig. 2 presents the values of maximal expansion (Δl , per cent) caused by saturation with cathodic hydrogen in different conditions as a function of elongation to fracture measured in a tensile machine (A , per cent). There is considerable scattering of results but, nevertheless, this chart shows that there is a direct relationship between the degree of brittleness and the expansion of the wire as a result of impregnation with cathodic hydrogen.

A number of experiments were made to investigate the effect of atomic hydrogen, produced by electric discharge at low pressure and of molecular hydrogen at temperatures from 500 to 700°C. No expansion of the wire could be observed in these conditions. Only when the iron wire was impregnated with cathodic hydrogen, could measurable changes be detected in its dimension.

Evaluation of those changes enabled us to estimate the lower limit of pressure of atomic hydrogen which acts probably on the surface of the

working cathode immersed in a solution containing such compounds as thiourea, hydrogen sulphide or arsenic oxide. In order to elongate the wire, annealed at 900°C., so that the change of length Δl will be 0.43 per cent (maximal expansion of this wire according to Fig. 1) we have to apply a strain of 14 kG per sq. mm. or 1400 kG per sq. cm. Since the wire begins to expand immediately after commencement of electrolysis, the actual pressure of atomic H on the surface of the cathode must in these conditions considerably exceed the value of 1400 atm.

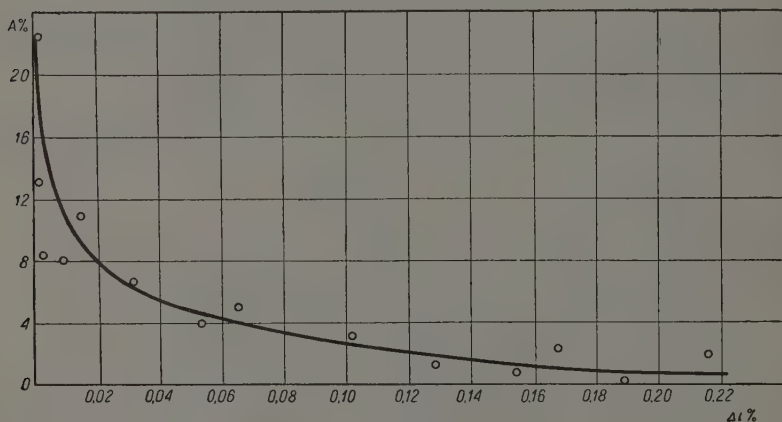


Fig. 2

We confirmed the observation made by Kuznetsov and Iofa [2] that the size of hydrogen bubbles which break away from the surface of the cathode depends on the composition of the electrolyte. The addition of thiourea, hydrogen sulphide or arsenic to the acid induces the formation of hydrogen bubbles which are smaller in comparison with those which arise in pure sulphuric acid. We noticed that when dibenzyl sulphoxide was present, the bubbles were much bigger than those in pure acid.

The pressure p required to produce gas bubbles in the liquid as defined by the well-known equation

$$p = \frac{2\sigma}{r}$$

enables us to calculate the bubble radius r for a given surface tension σ . For instance, if $p = 1400$ atm. and $\sigma = 73$ dyne cm.⁻¹, then $r \sim 10^{-7}$ cm. The actual conditions on the surface of a working cathode are much more complicated, since interfacial tensions, metal/liquid and metal/gas and electrostatic attraction should also be taken into consideration; but qualitatively one would expect that, in accordance with the observations made,

the factors occasioning formation of smaller bubbles should favour the diffusion of hydrogen into the cathode and vice versa.

Hence, these results suggest that the essential cause of the diffusion of cathodic hydrogen into iron is the formation of a very high value of atomic hydrogen pressure on the surface of the contact of the working electrode with the electrolyte. The value of that pressure seems to depend mainly on factors of an electrocapillary nature.

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The Dependence of Potential of a Cathodically Polarised Electrode on Electrolyte Structure Pt/HNO₃, Steel/HNO₃

by

S. MINC

Communicated by M. ŚMIAŁOWSKI at the meeting of May 18, 1953

The aim of the investigation described hereunder was to find the depolarising factor for the cathodic process on an electrode dipped in nitric acid in relation to acid concentration and current intensity. The method of investigation was based on the analysis of cathodic polarisation curves.

The cathodic polarisation curves were taken from measurements of changes of the examined electrode potential in relation to a saturated calomel electrode, at a temperature of 18°—20° C.

An electronic tube potentiometer ("Radiometer", type PHM 22) was used for the potential measurements. The constant and controlled current intensity was maintained by the use of a current stabiliser.

The cathodic and anodic parts of the measuring vessel were separated by porous glass. In order to avoid any unknown changes of potential at the liquid junction between a saturated solution of potassium chloride and the investigated nitric acid, the transitory system was used [1]; between the two mentioned solutions 0.01 n nitric acid was introduced. The change of diffusion potential at the liquid junction between the saturated solution of potassium chloride and the transitory 0.01 n nitric acid is negligible, but there remains a considerable potential difference between the examined nitric acid and the transitory one. The solution of nitric acid was connected with the transitory solution by an electrolytic key with a porous glass partition. One part of the key was filled with nitric acid and the other with transitory solution. By means of another key, filled with saturated potassium chloride solution with the addition of agar-agar, the transitory solution was connected with the saturated solution of potassium chloride. The calomel electrode was placed in the latter solution.

The measurements were made on the following electrodes:

- a) platinum electrode;
- b) chromium-nickel steel electrode (18—20% Cr, 9—10% Ni);
- c) chromium steel electrode (13—15% Cr).

All electrodes were carefully degreased. Steel electrodes were polished on emery paper. The polishing was performed first with medium-grain emery paper and then with ever finer grades, ending with No. 6/0. After polishing, the electrodes were kept for 24 hours in an exsiccator. So prepared they were dipped in the solution of nitric acid, and 20 minutes later the potential of the electrodes without current was measured. Then the electrodes were polarised with a current of constant intensity until the stabilization of the potential was obtained. The potential was considered stable when during a period of of ten minutes the potential fluctuations were less than 5 mV.

The results of the measurements are given in Table I, Table II and in the diagram (Fig. 1).

TABLE I

Values of platinum electrode potential during cathodic polarisation in nitric acid

Current intensity in mA	Concentration of nitric acid									
	1 m/l		2 m/l		3 m/l		4 m/l		5 m/l	
	E_c	E	E_c	E_d	E_c	E	E_c	E_d	E_c	E_d
0.60	173	170	196	200	221	220	243	750	254	801
1	147	144	170	165	195	185	217	740	228	794
2	112	106	135	130	160	147	182	727	193	785
3	66	70	89	90	114	105	136	706	147	770
10	31	40	54	59	79	70	102	688	113	761
20	-4	11	19	28	44	35	66	678	77	749
40	-39	-36	-16	-8	9	3	32	663	43	735
80	-74	-85	-51	-53	-26	-35	-4	650	7	721
160	-109	-345	-86	-128	-61	-90	-39	633	-28	703

E_c calculated potential in mV.

E_d experimentally determined potential in mV.

For a platinum electrode the theoretical potential during polarisation (E_c) was calculated with the aid of a simplified Volmer equation assuming the hydronium ion concentration in the layer close to the electrode to be the same as in the bulk of the electrolyte and taking under consideration — because of considerable overvoltage — only the reduction process:

$$E_c = E_H + A(l_g I - l_g c) + B$$

where

$$A = 0.116$$

B (average) = 471 (this constant was determined experimentally for 1 n nitric acid).

E_H — reversible potential of hydrogen electrode in the examined solution of acid.

I — intensity of polarising current.

c — analytical concentration of nitric acid.

TABLE II

The values of chromium-nickel steel electrode potential during cathodic polarisation in nitric acid

Current density in mA/cm. ²	Concentration of nitric acid				
	1 m/l	2 m/l	3 m/l	4 m/l	5 m/l
	potential in mV				
0	410	340	385	495	495
0.0025	—175	—120	290	345	455
0.005	—205	—155	255	325	425
0.01	—225	—175	210	290	390
0.02	—250	—195	145	275	355
0.03	—250	—200	95	—	—
0.04	—255	—205	90	230	305
0.05	—260	—210	60	—	—
0.06	—260	—210	45	—	—
0.08	—265	—215	25	185	245
0.10	—265	—220	25	150	225
0.15	—270	—225	—20	105	200
0.20	—275	—225	—55	55	165
0.25	—275	—230	—65	—	—
0.30	—280	—230	—80	0	135
0.35	—280	—230	—90	—	—
0.40	—280	—230	—100	—25	100
0.45	—285	—235	—105	—	—
0.50	—285	—235	—110	—40	82

From the data of Tables 1 and 2 and from Fig. 1 there results the conclusion that for a given current intensity ($I = \text{const.}$) and for nitric acid concentrations from 3 m/l. to 4 m/l. a violent potential change of polarised electrodes takes place. For concentrations weaker and stronger than these, the change of potential during polarisation is uniform. For weaker concentrations the potential change for each type of electrode is smaller

than for concentrations corresponding to a violent potential change (potential "jump"*)).

For a platinum electrode E_c it nearly equals the value of the electrode potential (E_d) determined experimentally for concentrations of nitric acid under 3 m/l.

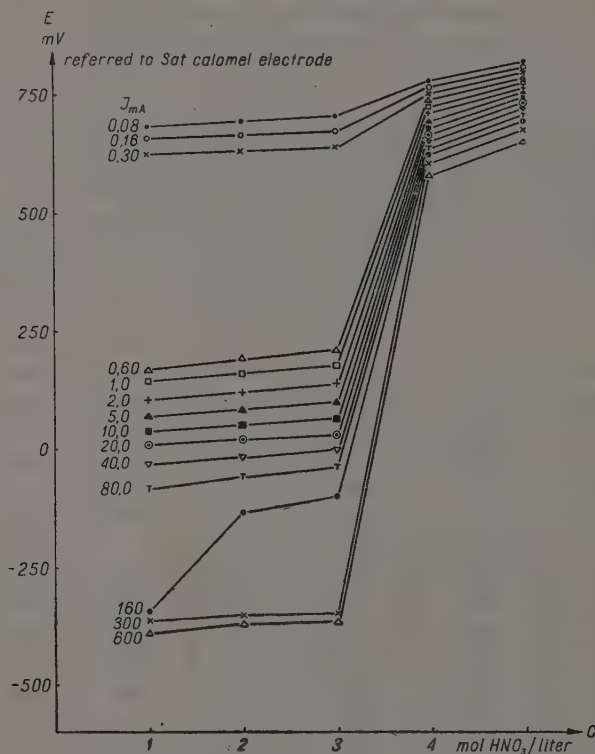
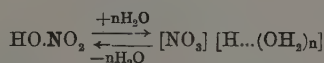


Fig. 1 Cathodic polarisation $E = f(\text{CHNO}_3)$ for $I = \text{const}$. Electrode: platinised platinum

It was established in the course of experiments that the "jump" of potential was accompanied by the formation of brown nitric oxides on the cathode. This formation was then observed with increased concentrations of nitric acid. For an electrode potential of about -270 mV and less, an evolution of gaseous hydrogen was clearly noted.

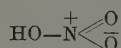
*) An analogous phenomenon is observed for a chromium steel electrode, but data is not given here due to the difficulties connected with determination of potential during the polarisation of this electrode.

From the data and observations given above the conclusion to be drawn is that during cathodic polarisation of nitric acid there exist two types of depolarisers, their action being mainly determined by acid concentration and partly by the material of the electrode. The conclusion that the type of depolarisation in nitric acid depends on its concentration would appear to be confirmed by the well known fact that in nitric acid there exists a state of tautomeric equilibrium between the pseudo form and the acid form [2], [3].



According to the investigations in Raman effect in nitric acid, the equilibrium between those two forms depends on acid concentration, so that in more concentrated acid the equilibrium shifts to the side of the pseudo form [4], [5].

The pseudo form of nitric acid begins to play the main part as a depolariser during polarisation at acid concentrations of 3-4 m/l. depending on the material of the electrode. At these concentrations the pseudo form becomes the main acceptor of electrons from the cathode. When they are close to the cathode, the molecules of the pseudo form of nitric acid



are electrically polarised under the influence of the electric field, and the bond between the HO and NO₂ groups is broken, giving a hydroxyl ion and a cation NO₂⁺. The latter takes an electron from the cathode giving nitrogen dioxide. $\text{N}\begin{array}{l} \text{O} \\ \text{O} \end{array}$ [6] (~~~single electron bond). This is confirmed, as mentioned above, by the evolution of brown nitric oxides.

Such a mode of depolarisation is more effective than hydrogen depolarisation (higher rate of acceptance of electrons), because the activation energy of the whole process (height of potential barrier) for homeopolar molecules is lower than for ions. The process does not take as much energy for dehydration as in the case of hydrogen depolarisation and so the potential of the electrode jumps on the passage of a definite concentration of the pseudo form.

Evolved NO₂ (as if *in statu nascendi*) has considerable oxidising properties.

An analogous course of events in the case of platinum and steel electrodes proves the importance of the electrolyte structure in the electrode process.

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TABLE DES MATIÈRES

Mathématique

T. Ważewski, Sur l'évaluation du nombre des paramètres essentiels dont dépend la famille des intégrales d'un système d'équations différentielles ayant une propriété asymptotique	3
J. Szarski et T. Ważewski, Sur une méthode de comparaison des équations hyperboliques aux dérivées partielles du second ordre avec les équations différentielles ordinaires :	6
Z. Mikołajska, Sur les mouvements asymptotiques d'un point matériel mobile dans le champ de forces repoussantes.	11
T. Ważewski, Sur une relation entre la façon de la mise en équation du problème physique et la notion des solutions généralisées des équations aux dérivées partielles du second ordre.	79
K. Kuratowski et H. Steinhaus, Une application géométrique du théorème de Brouwer sur les points invariants	83
K. Borsuk, An Application of the Theorem on Antipodes to the Measure Theory	87
K. Borsuk, Concerning the Cartesian Division by Manifold	91
K. Zarankiewicz, The Solution of a Certain Problem on Graphs of P. Turan	167
R. Sikorski, On Multiplication of Determinants in Banach Spaces	219
Z. Szmydt, Sur la structure de l'ensemble engendré par les intégrales tendant vers le point singulier du système d'équation différentielles	223
H. Rasiowa and R. Sikorski, On Satisfiability and Decidability in Non-Classical Functional Calculi	229
S. Mrówka, Solution d'un problème d'Urysohn concernant les espaces métriques universels	233
M. Fisz, The Limiting Distributions of Sums of Arbitrary Independent and Equally Distributed r -point ($r \geq 2$) Random Variables	235
A. Mostowski, A Lemma Concerning Recursive Functions and its Application	277

Astronomie

T. Banachiewicz, Occultation d'une Étoile fondamentale par le II Satélite de Jupiter le 20 Novembre 1952 (Annonce)	169
--	-----

Physique Théorique

J. Dąbrowski, Angular Correlations of Three Successive Gamma Quanta	14
L. Infeld, On the Use of an Approximation Method in Dirac's Electrodynamics	18
J. Werle, A New Approximation Method for the Meson Field Theory	23
W. Królikowski, Directional Correlations for Simultaneous Two-Quanta Processes	27

J. Plebański, Nonlinear Electrodynamics and Elementary Laws	34
J. Werle, On Mutual Nucleon-Nucleon Interaction through Meson Fields	95
L. Infeld, An Electronic Cloud in a Homogeneous Electric and Magnetic Field According to Dirac's Theory	99
J. Werle, An Application of a New Approximation Method to Quantum Calculations in the Meson Theory of Nuclear Forces	173
J. Werle, The Problem of "Equivalent" Potentials in Classical Equations of Motion	281

Physique Expérimentale

S. Pieńkowski, Radioactivité d'un groupe de phosphorites polonaises I.	39
M. Danyasz and J. Pniewski, Delayed Disintegration of a Heavy Fragment Emitted in Nuclear Explosion	42
J. A. Janik, The Scattering of Slow Neutrons by Liquids. I. Experiments with CH_3OH and CH_3I	45
A. Z. Hryniewicz, On the Deviation from the Quadratic Dependence on the Atomic Number of the Cross-Sections for Pair Production	49
M. D. Kunisz, Determination of the Relative Intensities in the Triplet $4d^3D - 4p^3P^0$ in Zn I Spectrum	52
K. Rosiński, Extinction thermique de fluorescences des solutions de biacène	55
M. Wielowiejska, On the Application of the Nuclear Emulsion Method to the Determination of the Absorption Coefficients of Slow Neutrons	60
Z. Wilhelmi, R. Brunsz and C. Dąbrowski, Some New Nuclear Reactions Produced in Tin by Fast Neutrons	105
K. Grotowski, A. Z. Hryniewicz and H. Niewodniczański, Effect of Thermionic Emission at Room Temperatures in Photosensitive Geiger-Müller Tubes	109
Z. Małkowski, Electronic and Vibrational Energy of Tetrahydrofluorocyclene in Benzene Solution	113
L. Sosnowski and M. Chmielewski, Response Time of Photoconductivity of Lead Selenide	119
H. Chęcińska, Photoconductive and Photovoltaic Layers of Lead Selenide	123
B. Makiej, Experimental Evidence that 90Y is not a Pure Beta-Emitter	127
M. Danyasz, An Example of V_1^0 -Decay Recorded in Photographic Emulsion	177
A. Wolska, Photo-Conductive and Photo-Voltaic Thallous Sulphide Layers	179
T. Piwkowski, Photo-Sensitive Lead Sulphide Layers with New Properties	185
J. Auleytner, The X-Ray Investigation of a Group of Fossil Rubbers	189
Z. Małkowski, On the Monochromatical Excitation of the Fluorescence in Tetrahydrofluorocyclene Solution	287
H. Niewodniczański and M. Wielowiejska, 3.20 MeV Radiation of ThD Determined by the Photographic Emulsion Technique	293

Chimie

W. Świątosławski, Classification of Negative Azeotropes XIV	63
W. Świątosławski, On Ternary Positive-Negative Azeotropes XV	66
W. Świątosławski, A Method for Determining the Composition and the Boiling Point of Ternary Positive-Negative Azeotropes XVI	70

T. Urbański, B. Skowrońska-Serafin, H. Dąbrowska and J. Janowska, On Reactions of Aromatic Amines with Cyanguanidine. Formation of Aryl-Derivatives of Amidine-Urea and their Transformation into Carbanilides	74
W. Trzebiatowski and B. Staliński, Magnetic Properties of Titanium Hydrides	131
B. Kamiński, Z. Było and B. Waligóra, Properties of the Antimony Microelectrode in Aqueous Alcoholic Solutions	137
B. Waligóra and Z. Było, Electrometric Adsorption Analysis of Strychnine and Brucine. Potentiometric Chromatography	143
T. Penkala, Binary Eutectics Formed by One Component with a Series of Homologues	149
T. Penkala, Binary Solid Solutions and Eutectic Mixtures Formed by One Component with Representatives of a Series of Homologues	151
M. Śmiałowski and Z. Szklarska-Śmiałowska, Adsorption of Dibenzyl Sulphoxide on Metals	155
M. Śmiałowski and Z. Szklarska-Śmiałowska, Evaluation of Diffusion of Hydrogen into Iron by Observation of Linear Expansion of a Sample	159
J. Kamecki and T. Drwal, Phosphate Coatings on Zinc and Its Alloys. I. Phosphate Treatment of Zinc in $Mn(H_2PO_4)_2$ Solutions	195
W. Świętosławski, Coal Tar as a Typical Polyazeotropic Mixture I	201
T. Urbański, On the Structure of Some Aliphatic Nitrocompounds	239
B. Kamiński and B. Waligóra, Electrometric Adsorption Analysis of the Alkaloids of the Poison Nut (<i>Strychnos Nux vomica</i>) on Aluminium Oxide. Potentiometric Chromatography	245
B. Kamiński and Z. Było, Electrometric Adsorption Analysis of the Alkaloids of the Poison Nut (<i>Strychnos Nux vomica</i>) on Charcoal. Potentiometric Chromatography	251
I. Chmielewska and J. Cieślak, Yangonin and Pseudoyangonin: Two Isomeric Ethers of Yangonolactone	257
B. Kamiński, K. Puchałka and Z. Doliński, The Application of the Antimony Microelectrode to Potentiometric Chromatography in Mixed Solvents of Benzene, Alcohol and Water	297
B. Kamiński and K. Puchałka, The Separation of Atropine and Hyoscyamine by the Potentiometric Chromatographic Method	305
B. Jeżowska-Trzebiatowska, J. Nawojcka and M. Wrońska, The Mechanism of Reduction of $KMnO_4$ by Concentrated KOH Solution	311
W. Trzebiatowski and B. Staliński, Magnetic Susceptibilities of Niobium Hydrides	317
T. Urbański, On Certain Hydroxamic Acids as Antitubercular Agents	319
S. Ślopek, On the Antitubercular Properties of 5-Bromosalicylhydroxamic Acid ("T40")	325
M. Śmiałowski and Z. Szklarska-Śmiałowska, The Mechanism of Diffusion of Cathodic Hydrogen into Iron	327
S. Minc, The Dependence of Potential of a Cathodically Polarised Electrode on Electrolyte Structure Pt/HNO_3 , $Steel/HNO_3$	333

Minéralogie

J. Tokarski, The Control of the Chemical Composition of Certain Industrial Products by the Method of Powder-Planimetric Analysis	261
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Géologie

J. Tokarski, The Problem of "Kalification" of Magmatic Rocks in the Region of Cracow	205
S. J. Thugutt, The Appearance of Peculiar Polymerism among Hydrated Alumino-Trisilicate Calcium Minerals	211
S. J. Thugutt, A Hydrodynamical Theory of the Origin of Pegmatite Veins	213
J. Tokarski, The Genesis and Systematic Position of Bentonites	267
K. Birkenmajer, Preliminary Revision of the Stratigraphy of the Pieniny Klippen-Belt Series in Poland	271

LISTE DES AUTEURS

Auleytner J.	189	Mrówka S.	233
Banachiewicz T.	169	Nawojcka J.	311
Birkenmajer K.	271	Niewodniczański H.	109, 293
Borsuk K.	87, 91	Penkala T.	149, 151
Brunsz R.	105	Pieńkowski S.	39
Było Z.	137, 143, 251	Piwkowski T.	185
Chęcińska H.	123	Plebański J.	34
Chmielewska I.	257	Pniewski J.	42
Chmielewski M.	119	Puchałka K.	297, 305
Cieślak J.	257	Rasiowa H.	229
Danysz M.	42, 177	Rosiński K.	55
Dąbrowska H.	74	Sikorski R.	225, 229
Dąbrowski C.	105	Skowrońska-Serafin B.	74
Dąbrowski J.	14	Sosnowski L.	119
Doliński Z.	297	Staliński B.	131, 317
Drwal T.	195	Steinhaus H.	83
Fisz M.	235	Szarski J.	6
Grotowski K.	109	Szklarska-Śmiałowska Z.	155, 159
Hryniewicz A. Z.	49, 109	Szmydt Z.	223
Infeld L.	18, 99	Ślopek S.	325
Janik J. A.	45	Śmiałowski M.	155, 159, 327
Jankowska J.	74	Świętosławski W.	63, 66, 70, 201
Jeżowska-Trzebiatowska B.	311	Thugutt S. J.	211, 213
Kamecki J.	195	Tokarski J.	205, 261, 267
Kamiński B.	135, 137, 251 297, 305	Trzebiatowski W.	131, 317
Królikowski W.	27	Urbański T.	74, 239, 319
Kunisz M. D.	52	Waligóra B.	137, 143, 245
Kuratowski K.	83	Ważewski T.	3, 6, 79
Makiej B.	127	Werle J.	23, 95, 281
Małkowski Z.	113, 287	Wielowiejska M.	60, 293
Mikołajska Z.	11	Wilhelmi Z.	105
Minc S.	333	Wolska A.	179
Mostowski A.	277	Wroniska M.	311
		Zarankiewicz K.	167

ERRATA

Page	Ligne	Au lieu de	Lire
20 ₆		$= A_{k,00} - A_{0,k0}$ $-2l-3 \quad -2l-3$	$= A_{k,00} - A_{0,k0}$ $2l+1 \quad 2l+1$
33 ⁸		$\frac{1}{(j-\frac{1}{2})(j+\frac{1}{2})(j+\frac{3}{2})}$	$\frac{1}{(j-\frac{1}{2})(j+\frac{1}{2})(j+\frac{3}{2})}$
42 ₇		Mev.	Gev.
67 ₁₁		Az	t_{Az}
67 ₅		$t_H A z_{-Az}$	$t_H t_{Az} t_{-Az}$
68 ¹⁶		weak for	weak for this reason
68 ₇		component A	component H
70 ₁₆		these azeotropes	these azeotropes, a new method
71 ₁₃		maximum	minimum
71 ₁		minimum	maximum
100 ⁴		$-V_0 \left(1 - \frac{x}{d}\right)^{1/2}$	$-V_0 e \left(1 - \frac{x}{d}\right)^{1/2}$
102 ⁴		$\varrho \equiv 0$	$\varrho = 0$
102 ₇		$\left[\frac{H}{2} \left(\varrho + \frac{\beta}{\varrho}\right)\right]^2$	$e^2 \left[\frac{H}{2} \left(\varrho + \frac{\beta}{\varrho}\right)\right]^2$
102 ₁₁		$+\beta\varphi + W(\varrho)$	$+\frac{H}{2}\beta\varphi + W(\varrho)$
103 ²		$v_{\varrho,\varrho} = W_{,\varrho\varrho} = 0$	$k v_{\varrho,\varrho} = W_{,\varrho\varrho} = 0$
103 ⁹		$+\left(\lambda_{,z} = 0\right)_{\varrho=R}$	$+A_2(\lambda_{,z} = 0)_{\varrho=R}$
103 ⁹		$+k\lambda_{,z} = 0$	$+k v_2 \lambda_{,z} = 0$
103 ₁₇		$\dot{S} = \omega$	$\dot{\varphi} = \omega$
103 ₅		$+\frac{1}{2} m v_z^2 t$	$+\frac{1}{2} k v_z^2 t$
103 ₂		$\frac{H}{2} \varrho^2 \omega \cos^{-2}(\omega t)$	$\frac{H}{2} \varrho^2 \omega \cos^{-2}(\omega t) + \frac{1}{2} k v_z^2$
103 ₂		$A_{\varphi} = \frac{H}{2} \varrho$	$A_{\varphi} = \frac{H}{2} \varrho$

Page Ligne	Au lieu de	Lire
149	Fig. 3	Fig. 3 de la page 151
151	Fig. 3	Fig. 4 de la page 152
152	Fig. 4	Fig. 3 de la page 149
156 (Fig. 1 et 2)	—	Adsorption g/g (sur l'axe des ordonnées) Concentration mol/kg. (sur l'axe des abscisses)
156 (Fig. 1)	20° C	40° C
157 ^a	0.5 kcal	— 0.5 kcal
157 ^a	1.7 kcal	— 1.7 kcal
236 ₂	$\frac{e^{-\lambda j}}{j!}$	$\frac{e^{-\lambda} \lambda^j}{j!}$
237 ^e	$(l - p_{n1})$	$(1 - p_{n1})$
237 ^e	$F(z)$	$F_n(z)$
237 _e	p_{n1}	p_{n1}
237 ₁	$F(z)$	$F_n(z)$
237 ₁ ⁸	$e^{-\frac{f}{z}}$	$e^{-\frac{f}{2}}$
240 (Fig. 1)	$m/\mu\lambda$	$m/\mu\lambda$
241 ¹⁷	(X), (base)	(IV), (V), (X) bases
241 ₂	$\begin{array}{c} \diagdown \text{CH}_2 - \text{NH}_2 \\ \text{Cl} \end{array}$	$\begin{array}{c} \diagdown \text{CH}_2 - \text{NH}_2^+ \\ \text{Cl}^- \end{array}$
312 ₉	=	$\leftarrow$ $\rightarrow$
312 ₁₄	=	$\leftarrow$ $\rightarrow$
325 ₁₄	apium	avium